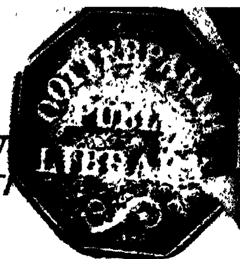


CHEMISTRY,

INORGANIC AND ORGANIC

WITH EXPERIMENTS

BY

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EXTRACTS

FROM THE

PREFACE TO THE FIRST EDITION.

THIS work is designed to give a clear and simple description of the elements and their principal compounds, and of the chemical principles involved in some of the most important branches of manufacture. Keeping this in view, I have employed as few technical terms as possible, especially at the commencement, so that the student may glide into Chemistry without having first to toil through a difficult chapter on the terminology of the science, which he can never appreciate until he has become acquainted with the examples which serve to illustrate its application.

Convinced, by experience, of the great assistance afforded to the learner by referring him to a simple illustrative experiment, I have introduced, generally in smaller type, a description, and in most cases a wood-engraving, of the experiments which I have found most useful in illustrating lectures, hoping that these may prove of service in fixing the attention of the student, and may assist those who are desirous of performing such experiments for their own instruction, or for that of a class.

In general, English weights and measures, and Fahrenheit thermometric degrees, have been employed, as conveying more clearly to the beginner the absolute values expressed, since the mental effort of converting what must still be called the Continental systems, slight though it be, might have the effect of diverting the attention of the reader from the chemical question under consideration. The various calculations have been conducted in the simplest arithmetical form, because the more compendious

algebraical expressions are not so generally intelligible, and when the principle is once understood, a general algebraical formula for the calculation is easily constructed by the learner.

The special attention devoted to Metallurgy and some other branches of Applied Chemistry, will render the work useful to those who are being educated for employment in manufacture.

The military student will find more than the usual space allotted to the chemistry of the various substances employed in warlike stores.

C. L. B.

PREFACE TO THE SECOND EDITION.

DURING the five years which have elapsed since the publication of the First Edition of this work, the adoption of the atomic system of notation has become so general among English chemists that I have felt obliged to employ it in the present edition. This change has rendered it necessary to commence the study of the non-metallic elements with Hydrogen instead of Oxygen, a course attended with some disadvantage to beginners, because Hydrogen is prepared and studied by processes which are strictly technical, whereas Oxygen is known in a free state in the atmosphere, where we constantly witness its chemical action upon other bodies. Moreover, the circumstance that the science of chemistry originated in the careful study of the phenomena of combustion towards the end of the last century, appears to me greatly in favour of our commencing a course of elementary chemistry from that point. Since, however, Hydrogen is the chemical unit of the atomic system, whilst Oxygen is a diatomic element, I have found it absolutely necessary to assign to this latter the second place. Indeed, to teach the atomic system in its integrity, it would be necessary to postpone the study of Oxygen until all the monatomic elements had been disposed of, and thus to defer, till a late period, the consideration of the processes of combustion which awaken the interest of even the least observant student.

Although I thoroughly appreciate the beauty and harmony of the atomic system, and acknowledge the immense assistance which it has afforded in research, I contemplate with regret its almost

universal adoption by chemical teachers in this country, since it involves the necessity of propounding the difficult hypothesis of the finite divisibility of matter at the commencement of a study which has been recommended to the student as strictly experimental, and as affording a mental relief from the abstractions of mathematics. Even if it be alleged that it is not necessary to mention atoms to beginners, but that the teacher may confine himself, as is now sometimes the case, to combining proportions, the combining weight of hydrogen in water must be represented as 2; a perplexing, and at this stage totally unnecessary inquiry being suggested to the mind of the pupil, why it is set down as 1 in the lists of combining weights.

The numerous failures in Chemistry at the examinations now so much in vogue, appear to indicate the difficulty experienced by the immature minds of the young in laying hold of the ideas of atomicity and quantivalence which pervade many of the questions, whereas the mutual relations between the elements and their compounds, which are easily impressed on the mind by experiment, and involve as much Chemistry as the young student can grasp, are treated as of subordinate importance.

The tendency to regard Chemistry as a modified Algebra has become so great since the general introduction of the atomic system, that it is not uncommon for teachers in schools to prepare the pupils for examination in Chemistry, who have themselves never had the opportunity of learning how to conduct the simplest chemical operation.

To acquire a knowledge of the rudiments of Chemistry by personal observation, has, without doubt, a very beneficial effect; but to *get up* a number of formulæ and equations, with the sole object of gaining a certain number of marks at examination, altogether defeats the object with which Chemistry should be introduced into a system of liberal education.

In this edition I have endeavoured to preserve, as far as possible, the simple and experimental character of the work, and at the same time to employ formulæ in harmony with those now generally used. The nomenclature has undergone very little change, since there is by no means a general agreement upon this subject; and I deem it of the greatest importance that the names by which

chemical compounds are known in common life should be kept before the student in a chemical treatise.

The attention of the student is called to the Table of Contents, which has been drawn up to serve the purpose of an abstract, by which he may examine himself upon each paragraph of the book. The Index is also a dictionary of the most important formulæ, in which either the name of a compound may be referred to, in order to find its formula, or the formula may be sought when it is desired to ascertain the compound to which it belongs.

C. L. B.

KING'S COLLEGE, LONDON,
July 1872.

*** In the following pages, the smaller type contains not only the descriptions of experiments, but all such matter as would be of less importance to a student desiring only a general knowledge of the subject without going into details.

A Table of Atomic Weights will be found at page 628.

TABLE OF CONTENTS.

CHEMISTRY OF THE METALS.

ORGANIC CHEMISTRY.

INTRODUCTION.

1. CHEMISTRY describes the properties of the different particles of which all kinds of matter are composed, and teaches the laws which regulate their union with, or separation from, each other.

Matter is anything which possesses weight. Matter is chemically divided into two great classes—elements and compounds.

An ELEMENT is that which has not been found divisible into more than one kind of matter.

A COMPOUND consists of two or more elements held together by chemical attraction.

CHEMICAL ATTRACTION is the force which causes different kinds of matter to unite, in order to form a new kind of matter.

Chemical Combination is the operation of chemical attraction.

Chemical Decomposition is the separation of two or more kinds of matter previously held together by chemical attraction.

2. The elements known at present are sixty-four in number, and are divided into metallic and non-metallic elements.

The *Non-Metallic Elements* are (15).

Oxygen. Hydrogen. Nitrogen. Carbon. Boron. Silicon.	Sulphur. Selenium. Tellurium. Phosphorus. Arsenic.*	Fluorine. Chlorine. Bromine. Iodine.

The *Metals* are (49).

Cæsium. Rubidium. Potassium. Sodium. Lithium. Barium. Strontium. Calcium. Magnesium.	Aluminum. Glucinum. Zirconium. Thorinum. Yttrium. Erbium. Terbium. Cerium. Lanthanum. Didymium. Niobium.	Zinc. Nickel. Cobalt. Iron. Manganese. Chromium. Cadmium. Uranium. Indium.	Copper. Bismuth. Lead. Thallium. Tin. Titanium. Tantalum. Molybdenum. Tungsten. Vanadium. Antimony.	Mercury. Silver. Gold. Platinum. Palladium. Rhodium. Ruthenium. Osmium. Iridium.

The strict definition of a metal will be given hereafter.

Many of these elements are so rarely met with, that they have not

* In many English chemical works arsenic is classed among the metals, which it resembles in some of its properties.

received any useful application, and are interesting only to the professional chemist. This is the case with selenium and tellurium, among the non-metallic elements, and with a large number of the metals.

The following list includes those elements with which it is important that the general student should become familiar, together with the symbolic letters by which it is customary to represent them, for the sake of brevity, in chemical writings.

Non-Metallic Elements of practical importance (13).

Oxygen,	O	Sulphur,	S	Fluorine,	F
Hydrogen,	H	Phosphorus,	P	Chlorine,	Cl
Nitrogen,	N	Arsenic,	As	Bromine,	Br
Carbon,	C			Iodine,	I
Boron,	B				
Silicon	Si				

Metallic Elements of practical importance (26).

Potassium,	K	(*Kalium.*)	Cadmium,	Cd	
Sodium,	Na	(*Natrium.*)	Uranium,	U	
Barium,	Ba		Copper,	Cu	(*Cuprum.*)
Strontium,	Sr		Bismuth,	Bi	
Calcium,	Ca		Lead,	Pb	(*Plumbum.*)
Magnesium,	Mg		Tin,	Sn	(*Stannum.*)
Aluminum,	Al		Titanium,	Ti	
			Tungsten,	W	(*Wolframium.*)
Zinc,	Zn		Antimony,	Sb	(*Stibium.*)
Nickel,	Ni				
Cobalt,	Co		Mercury,	Hg	(*Hydrargyrum.*)
Iron,	Fe	(*Ferrum.*)	Silver,	Ag	(*Argentum.*)
Manganese,	Mn		Gold,	Au	(*Aurum.*)
Chromium,	Cr		Platinum,	Pt	

Although the 39 elements here enumerated are of practical importance, many of them derive their importance solely from their having met with useful applications in the arts. The number of elements known to play an important part in the chemical changes concerned in the maintenance of animal and vegetable life is very limited.

Elements concerned in the Chemical Changes taking place in Life.

Non-Metallic.		*Metallic.*	
Oxygen.	Sulphur.	Potassium.	Aluminum.
Hydrogen.		Sodium.	
Nitrogen.	Phosphorus.		Iron.
Carbon.		Calcium.	Manganese.
	Chlorine.	Magnesium.	
Silicon.	Iodine.		

These elements will, of course, possess the greatest importance for those who study Chemistry as a branch of general education, since a knowledge of their properties is essential for the explanation of the simplest chemical changes which are daily witnessed.

The student who takes an interest in the useful arts will also acquaint himself with the remainder of the 39 elements of practical importance,

whilst the mineralogist and professional chemist must extend his studies to every known element.

By far the greater proportion of the various materials supplied to us by animals and vegetables consists of the four elements—oxygen, hydrogen, nitrogen, and carbon; and if we add to these the two most abundant elements in the mineral world, silicon and aluminum, we have the six elements composing the bulk of all matter.

The symbols of the chemical elements represent, as will be explained hereafter, definite relative proportions by weight, or chemical units of the elements; thus O represents a chemical unit of oxygen, and C a chemical unit of carbon.

To express a number of chemical units of any element, it is usual to place a numeral below and to the right of the symbol; thus O_2 represents two chemical units of oxygen.

The mere contact or mixture of substances is expressed by the sign +; thus, $C + O_2$ implies that a chemical unit of carbon has been brought into contact with two chemical units of oxygen.

But when the elements are chemically combined they are placed side by side; thus CO_2 represents carbonic acid gas; CaO represents lime.

To indicate that two compound bodies have combined to form a new compound, a point or a comma is placed between them; thus $CaO.CO_2$ represents the compound of lime with carbonic acid, known as carbonate of lime or chalk.

3. Compound substances are commonly classified by the chemist into *Organic* and *Inorganic* compounds; and although it is impossible strictly to define the limits of each class, the division is a convenient one for the purposes of study.

Organic substances may be defined as those for which we are indebted to the operation of animal or vegetable life, such as starch, sugar, &c.

Inorganic substances are obtained from the mineral world without the intervention of life; as common salt, alum, &c.

Organic substances always contain carbon, generally also hydrogen and oxygen, and very frequently nitrogen.

INORGANIC CHEMISTRY.

CHEMISTRY OF THE NON-METALLIC ELEMENTS, AND THEIR COMPOUNDS.

WATER.

4. A century has not yet elapsed since water ceased to be regarded as an elementary form of matter. It was first resolved into its constituent elements, hydrogen and oxygen, by subjecting it to the influence of the *voltaic current*, which decomposes or *analyses* the water by overcoming the chemical attraction by which its elements are held together.

An arrangement for this purpose is represented in fig 1.

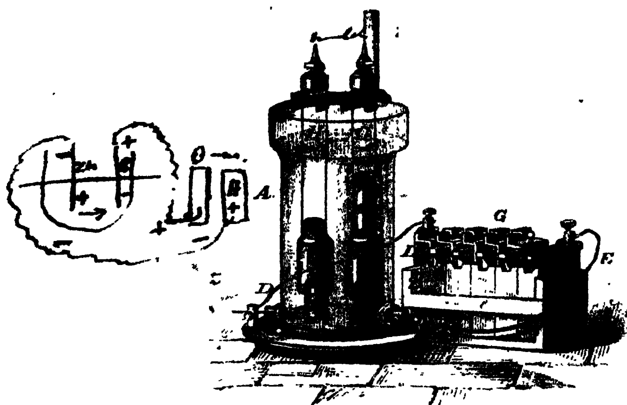


Fig. 1.—Electrolysis of water.

The glass vessel A contains water, to which a little sulphuric acid has been added to increase its power of conducting electricity, for pure water conducts so imperfectly that it is decomposed with great difficulty. B and C are platinum plates bent into a cylindrical form, and attached to stout platinum wires, which are passed through corks in the lateral necks of the vessel A, and are connected by binding screws with the copper wires D and E, which proceed from the galvanic battery G. H and O are glass cylinders with brass caps and stop-cocks, and are enlarged into a bell-shape at their lower ends for the collection of a considerable volume of gas. These cylinders are filled with the acidulated water, by sucking out the air through the opened stop-cocks; on closing these, the pressure of the air will of course sustain the column of water in the cylinders. G is a Grove's battery, consisting of five cells or earthenware vessels (A, fig. 2) filled with diluted sulphuric acid (one measure of oil of vitriol to four of water). In each of these cells is placed a bent plate of zinc (B), which has been

amalgamated or rubbed with mercury (and diluted sulphuric acid) to protect it from corrosion by the acid when the battery is not in use. Within the curved portion of

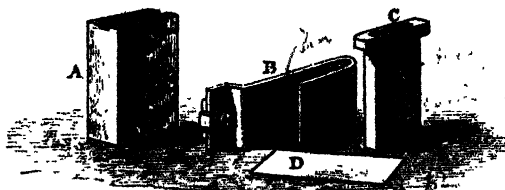


Fig. 2.

this plate rests a small flat vessel of unglazed earthenware (C), filled with strong nitric acid, in which is immersed a sheet of platinum foil (D. The platinum (D) of each cell is in contact, at its upper edge, with the zinc (B) in the adjoining cell (fig. 3), so that at one end (P, fig. 1) of the battery there is a free platinum plate, and at the other (Z) a free zinc plate. These plates are connected with the wires D and E by means of the copper plates L and K, attached to the ends of the wooden trough in which the cells are arranged. The wire D (fig. 1), which is connected with the last *zinc* plate of the battery, is often called the "*negative* pole;" whilst E, in connexion with the last *platinum* plate, is called the "*positive* pole."

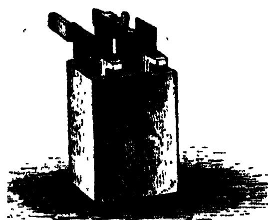


Fig. 3.

When the connexion is established by means of the wire D and E with the "decomposing cell" (A), the "galvanic current" is commonly said to pass along the wire E to the platinum plate C, through the acidulated water in the decomposing cell, to the platinum plate B, and thence along the wire D back to the battery.

A very elegant apparatus (fig. 4) has been devised by Dr Hofmann for exhibiting the decomposition of water by the galvanic current. The water displaced by the gases accumulating in the tubes *h*, *o* collects in the bulb *b* upon the longer branch, and exerts the pressure necessary to force the gases out when the stop-cocks are opened. The stop-cocks, being made of glass, are not corroded by the acid.

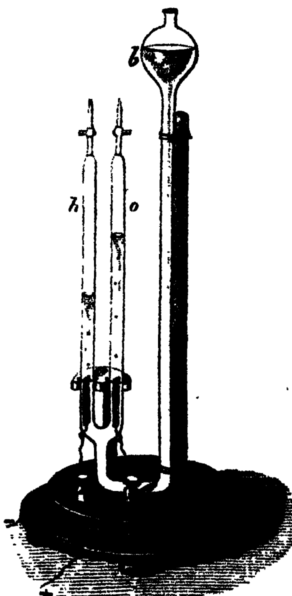


Fig. 4.—Electrolysis of water.

5. During this "passage of the current" (which is only a figurative mode of expressing the transfer of the electric influence), the water intervening between the plates B and C is decomposed, its hydrogen being attracted to the plate B (negative pole), and the oxygen to the plate C (positive pole). The gases can be seen adhering in minute bubbles to the surface of each plate, and as they increase in size they detach themselves, rising through the acidulated water in the tubes H and O, in which the two gases are collected.

Since no transmission of gas is observed between the two plates, it is evident that the H and O separated at any given moment from each plate do not result from the decomposition of one particle of water, but from

water lying between the plates P and Z before the "current" is passed, and B the state of the particles when the current has been established. P is (the positive pole) in connexion with the last platinum plate of the battery, and Z is (the negative pole) in connexion with the last zinc plate.

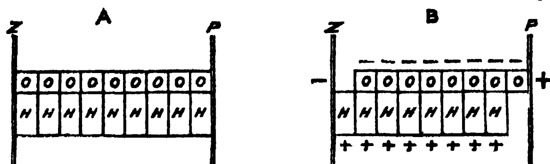


Fig. 5.

The signs + and – made use of in B refer to a common mode of accounting for the decomposition of water by the battery, on the supposition that the oxygen is in a negatively electric condition, and therefore attracted by the positive pole P; whilst the hydrogen is in a positively electric condition, and is attracted by the negative pole Z.

The decomposition of compounds by galvanic electricity is termed *electrolysis.** When a compound of a metal with a non-metal is decomposed in this manner, the metal is usually attracted to the (negative) pole in connexion with the zinc plate of the battery, whilst the non-metal is attracted to the (positive) pole connected with the platinum plate of the battery.

Hence the metals are frequently spoken of as *electro-positive* elements, and the non-metals as *electro-negative.*

6. If the passage of the "current" be interrupted when the tube H has become full of gas, the tube O will be only half full, since *water contains hydrogen and oxygen in the proportion of two volumes of hydrogen to one volume of oxygen.* When the wider portions of the tubes (fig. 1) are also filled, the two gases may be distinguished by opening the stop-cocks in succession, and presenting a burning match. The hydrogen will be known by its kindling with a slight detonation, and burning with a very pale flame at the jet; whilst the oxygen will very much increase the brilliancy of the burning match, and if a spark left at the extremity of the match be presented to the oxygen, the spark will be kindled into a flame.

Another method of effecting the decomposition of water by electricity consists in passing a succession of electric sparks through steam. It is probable that in this case the decomposition is produced rather by the intense heat of the spark than by its electric influence.

For this purpose, however, the galvanic battery does not suffice, since no spark can be passed through any appreciable interval between the wires of the battery,—a fact which electricians refer to in the statement that although the *quantity* of electricity developed by the galvanic battery is large, its *intensity* is too low to allow it to discharge itself in sparks like the electricity from the machine or from the induction-coil, which possesses a very high intensity, though its quantity is small.

7. The most convenient instrument for producing a succession of electric sparks is the *induction-coil,* by the aid of which the electric influence

* Ἤλεκτρον (amber—root of *electricity*); λύω, to loosen.

of even a single cell of the galvanic battery may be so accumulated as to become capable ef discharging itself in sparks, such as are obtained from the electrical machine.*

Fig. 6 represents the arrangement for exhibiting the decomposition of steam by the electric spark.

A is a half-pint flask furnished with a cork in which three holes are bored; in one of these is inserted the bent glass tube B, which dips beneath the surface of the water in the trough C.

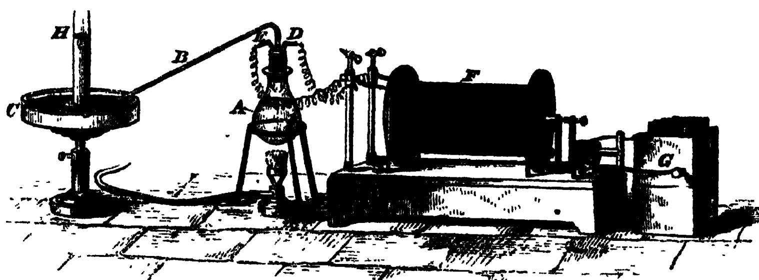


Fig. 6.—Decomposition of steam by electric sparks.

D and E are glass tubes, in each of which a platinum wire has been sealed so as to project about an inch at both ends of the tube. These tubes are thrust through the holes in the cork, and the wires projecting inside the flask are made to approach to within about $\frac{1}{16}$ inch, so that the spark may pass easily between them.

The flask is somewhat more than half filled with water, the cork inserted, and the tube B allowed to dip beneath the water in the trough; the wires in D and E being connected with the thin copper wires passing from the induction-coil F, which is connected by stout copper wires with the small battery G.

The water in the flask is boiled for about fifteen minutes, until all the air contained in the flask has been displaced by steam. When this is the case, it will be found that if a glass test-tube (H) filled with water be inverted† over the orifice of the tube B, the bubbles of steam will entirely condense, with the usual sharp rattling sound, and only insignificant bubbles of air will rise to the top of the test-tube. If now, whilst the boiling is still continued, the handle of the coil (F) be turned so as to cause a succession of sparks to pass through the steam in the flask, large bubbles of incondensable gas will accumulate in the tube H. This gas consists of the hydrogen and oxygen gases in *a mixed* state, having been released from their *combined* condition in water by the action of the electric sparks. The gas may be tested by closing the mouth of the tube H with the thumb, raising it to an upright position, and applying a lighted match, when a sharp detonation will indicate the recombination of the gases.‡

It has long been known that a very intense heat is capable of decomposing water. The temperature required for the purpose is below the melting point of platinum, as may be shown by the apparatus represented in fig. 7.

A platinum tube (*t*) is heated by the burner *b*, the construction of which is shown at the bottom of the cut. It consists of a wide brass tube, from which the coal gas issues through two rows of holes, between which oxygen is supplied through the holes in the narrow tube, brazed into a longitudinal slit between the two rows of holes in the gas tube. The oxygen is supplied from a gas-bag or gas-holder, with which the pipe (*o*) is connected.

The flask (*f*) containing boiling water is furnished with a perforated cork, carrying a brass tube (*a*), which slips into one end of the platinum tube, into the other end of

* For a description of the induction-coil, see Miller's "Elements of Chemistry," Part I. p. 575.

† The end of the tube B should be bent upwards and thrust into a perforated cork with notches cut down the sides. By slipping this cork into the neck of the test-tube, the latter will be held firmly.

‡ With a powerful coil, a cubic inch of explosive gas may be collected in about fifteen minutes.

which another brass tube (c) is slipped; this is prolonged by a glass tube attached by india-rubber, so as to deliver the gas under a small jar standing upon a bee-hive shelf in the trough.

The platinum tube is not heated until the whole apparatus is full of steam, and no

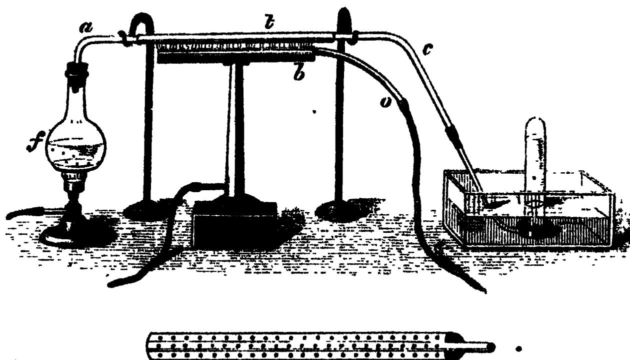


Fig. 7.—Decomposition of steam by heat.

more bubbles of air are seen to rise through the water in the trough; the gas-burner is then lighted, and the oxygen turned on until the platinum tube is heated to a very bright red heat; bubbles of the mixture of hydrogen and oxygen resulting from the decomposition of the water may then be collected in the small jar, and afterwards exploded by applying a flame.

8. The decomposition of water by the galvanic current proved that there are *two volumes of hydrogen combined with one volume of oxygen.*

Hydrogen is the lightest form of matter with which we are acquainted, and is therefore generally regarded as the chemical unit of weight and volume, *i.e., one part by weight of hydrogen occupies one volume.*

Oxygen is found to be sixteen times as heavy as hydrogen, that is, a given measure of oxygen weighs sixteen times as much as an equal measure of hydrogen.

Since the two volumes of hydrogen in water represent two parts by weight, the one volume of oxygen represents sixteen parts by weight.

Water is invariably found to contain exactly these proportions of its elements, illustrating the *law of definite proportions*, that a *given compound always contains the same elements in the same proportions.*

This law is characteristic of the force of chemical attraction, no such law being observed in the operation of either of the other forces of attraction by which the particles of matter are influenced, viz., those of gravitation, cohesion, electricity, and magnetism. To account for the existence of such a law limiting the operation of chemical attraction, it is necessary to refer to the theory of the atomic constitution of matter.

*Atomic Theory.**—All matter is composed of minute particles, which are incapable of being further subdivided, and are therefore called *atoms.*†

The atoms of the same element have all the same weight, but the atoms of different elements have different weights.

A compound form of matter results from the operation of chemical attraction between a definite number of atoms of each of the elements composing it.

* Θεωρία, a (mode of) viewing. † Ἄτομος, indivisible.

Thus, if each atom of oxygen is sixteen times as heavy as each atom of hydrogen, water, which contains 16 parts by weight of oxygen, and 2 parts by weight of hydrogen, must be composed of one atom of oxygen and two atoms of hydrogen, as indicated by the formula H_2O, the *atomic formula of water.* Since it is found that *all gases are expanded to the same extent by being heated to the same degree*, and *are contracted to the same extent by the application of equal amounts of pressure*, they must contain equal numbers of atoms in equal volumes.*

Hence, since water contains twice as many *volumes* of hydrogen as of oxygen, it contains twice as many *atoms* of hydrogen.

Very important evidence in favour of the atomic theory is derived from the consideration of the *specific heats* of the elementary forms of matter.

A given weight of hydrogen gas, in cooling down through one degree of the thermometer, gives out *sixteen* times as much heat as an equal weight of oxygen gas gives out in cooling down through one degree. Or, conversely, to raise the temperature of a given weight of hydrogen through one degree, requires sixteen times as much heat as would be required to raise the temperature of an equal weight of oxygen through one degree.

This is generally expressed by saying that *the specific heat of hydrogen is sixteen times that of oxygen.*

Hence, 16 parts by weight of oxygen, in cooling down through one degree, gives out as much heat as 1 part by weight of hydrogen. On the assumption, therefore, that the atom of oxygen is sixteen times as heavy as the atom of hydrogen, *the atoms of these elements are associated with equal amounts of heat*, a conclusion quite in harmony with the results of other physical observations. Unfortunately, the specific heats, like the specific volumes, of different substances, can only be compared when they are in the same physical condition, since the specific heat of a given substance varies accordingly as it is in the gaseous, liquid, or solid form, and since the greater number of the elements cannot be obtained in the gaseous state, it is not possible to compare their specific heats with that of hydrogen. Moreover, the determination of the specific heats of gases and vapours is attended with great difficulty, so that only oxygen and nitrogen have at present been shown by experiment to have the same *atomic heat* as hydrogen.

(Definition.—The atomic heat of an element is the product of its specific heat multiplied by its atomic weight.)

The atomic heat of hydrogen is 3·4090; those of oxygen and nitrogen are 3·48 and 3·41 respectively. The atomic heats of the solid elements are, as a rule, expressed by a number which is nearly double this, but the variations are so considerable (the discrepancy amounting in some cases to nearly $\frac{1}{12}$), that although the identity of the atomic heats is distinctly indicated, it cannot be said to have been satisfactorily established in all cases.

9. In the preceding experiments, the force of chemical attraction holding the particles of oxygen and hydrogen together in the form of water, has been overcome by the physical forces of heat and electricity. But water may be more easily decomposed by acting upon it with some element which has a sufficiently powerful chemical attraction for the oxygen of water to draw it away from the hydrogen.

No non-metallic element is capable of abstracting the oxygen from water at the ordinary temperature.

* Assuming, of course, that the atoms are placed at equal distances apart in the case of all gases.

Among the practically important metals, there are five which have so powerful an *attraction for oxygen* that it is necessary to preserve them in bottles filled with some liquid free from that element, such as petroleum, (composed of carbon and hydrogen), to prevent them from combining with the oxygen of the atmosphere. These metals are capable of decomposing water with great facility.

Metals which decompose water at the ordinary temperature.—Potassium, Sodium, Barium, Strontium, Calcium.

When a piece of potassium is thrown upon water, it takes fire and burns with a fine violet flame, floating about as a melted globule upon the surface of the water, combining with the oxygen, and producing, in the act of combination, enough heat to kindle the hydrogen as it escapes. The violet colour of the flame is due to the presence of a little potassium in the form of vapour. The same results ensue if the potassium be placed on ice. The water in which the potassium has been dissolved will be found soapy to the touch and taste, and will have a remarkable action upon certain colouring matters. Paper coloured with the yellow dye *turmeric* becomes brown when dipped in it, and paper coloured with *red litmus* (*archil*) becomes blue. Substances possessing these properties have been known from a very remote period as *alkaline* substances, apparently because they were first observed by the alchemists in the ashes of plants called *kali*.

The alkalies are among the most useful of chemical agents.

Definition of an alkali.—A compound substance, very soluble in water, turning litmus blue and turmeric brown.

These alkaline properties are directly opposed to the characters of sour or *acid** substances, such as vinegar or vitriol, which change the blue litmus to red.

When an acid liquid, such as vinegar (acetic acid) or vitriol (sulphuric acid), is added to an alkaline liquid, the characteristic properties of the latter are destroyed, the alkali being *neutralised*.

An acid substance may be known by its property of neutralising an alkali (either entirely or partly).

The minute investigation into the action of potassium upon water would require considerable manipulative skill. It would be necessary to weigh accurately the potassium employed, to evaporate the resulting solution in a silver basin (most other materials being corroded by the alkali), and after all the water had been expelled by heat, to ascertain the composition of the residue by a chemical analysis.

It would be found to contain, by weight, 1 part of hydrogen, 16 parts of oxygen, and 39 parts of potassium.

Since water contains 2 parts by weight of hydrogen, combined with 16 parts of oxygen, it is evident that the product of the action of potassium on water is formed by the substitution of 39 parts of potassium for 1 part of hydrogen.

It is found that whenever potassium takes the place of hydrogen in a compound, 39 parts of the former are exchanged for one of the latter, and this is generally expressed by stating that 39 is the *chemical equivalent* of potassium.

The *chemical equivalent of a metal* expresses the weight which is required to be substituted for one part by weight of hydrogen in its compounds.

* From ἀκή, a point, referring to the pungency or sharpness of the acid taste.

The action of potassium upon water is an example of the production of compounds by substitution of one element for another, a mode of formation which is far more common than the production of compounds by direct combination of their elements.

It is commonly assumed by chemists that the weight of an *atom* of potassium is 39 times that of an atom of hydrogen.

If the symbol K be taken to represent 39 parts by weight of potassium, its action upon water would be represented by the chemical equation



$$\underset{\text{Water.}}{H_2O} + K = \underset{\text{Caustic potash.*}}{KHO} + H.$$

Sodium has a less powerful attraction for oxygen than potassium, and does not usually take fire when thrown into cold water, although it is at once fused by the heat evolved in its combination with the oxygen. By holding a lighted match over the globule as it swims upon the water, the hydrogen may be kindled, when its flame is bright yellow from the presence of the sodium. The solution will be found strongly alkaline from the soda produced. By placing the sodium on a piece of blotting paper laid on the water, it may be made to ignite the hydrogen spontaneously, because the paper keeps it stationary, and prevents it from being so rapidly cooled by the water. Several cubic inches of hydrogen may easily be collected by placing a piece of sodium as large as a bean in a small wire-gauze box (A, fig. 8), and holding it under an inverted cylinder (B) filled with water and standing upon a bee-hive shelf.

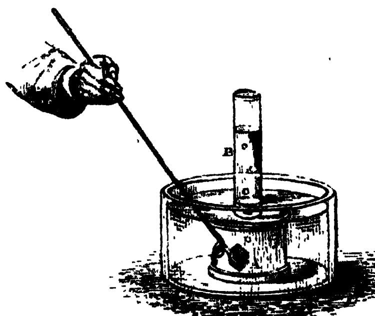
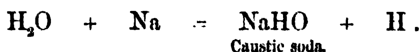


Fig. 8.

The product of the action of sodium upon water contains 1 part by weight of hydrogen, 16 of oxygen, and 23 of sodium, so that the 23 parts of sodium have been exchanged for, or been found chemically equivalent to, 1 part of hydrogen.

The atom of sodium is generally taken to be twenty-three times as heavy as the atom of hydrogen.

Taking the symbol Na to represent 23 parts by weight of sodium, its action on water would be expressed thus—



$$H_2O + Na = \underset{\text{Caustic soda.}}{NaHO} + H.$$

Barium, strontium, and calcium decompose water less rapidly than potassium and sodium.

The tendency of heat to separate the elements of water being known, it might be expected that metals which refuse to decompose water at the ordinary temperature, would be induced to do so if the temperature were raised, and accordingly magnesium and manganese, which are without action upon cold water, decompose it *at the boiling point*, disengaging hydrogen, and producing magnesia (MgO, a feebly alkaline earth) and oxide of manganese (MnO).

* Caustic, from καιω, to burn, in allusion to its corrosive properties; and potash, from its having been originally prepared from the washings of wood ashes boiled down in iron pots and decomposed by lime.

But the greater number of the common metals must be raised to a much higher temperature than this in order to enable them to decompose water. The following metals will abstract the oxygen from water at high temperatures, those at the commencement of the list requiring to be heated to redness (about 1000° F.), and the temperature required progressively increasing, until it attains whiteness for those at the end of the list.

Metals which decompose water at a temperature above a red heat.—Zinc, Iron, Chromium, Cobalt, Nickel, Tin, Antimony, Aluminum, Lead, Bismuth, Copper.

The *noble metals*, as they are called, which exhibit no tendency to oxidise in air, are incapable of removing the oxygen from water, even at high temperatures.

Metals which are incapable of decomposing water.—Mercury, Silver, Gold, Platinum.

HYDROGEN.

10. *Preparation of hydrogen.*—The simplest process, chemically speaking, for preparing hydrogen in quantity, consists in passing steam over red-hot iron. An iron tube (A, fig. 9) is filled with iron nails and fixed

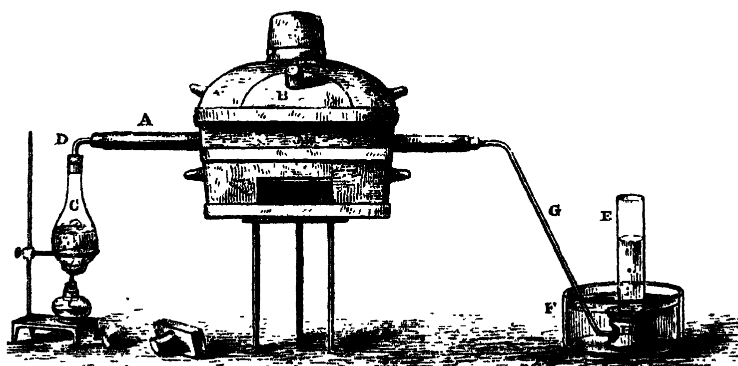


Fig. 9.—Preparation of hydrogen from steam.

across a furnace (B), in which it is heated to redness by a charcoal fire. A current of steam is then passed through it by boiling the water in the flask (C), which is connected with the iron tube by a glass tube (D) and perforated corks. The hydrogen is collected from the glass tube (G) in cylinders (E) filled with water, and inverted in the trough (F) upon the bee-hive shelf (H), the first portions being allowed to escape, as containing the air in the apparatus. The iron combines with the oxygen of the water to form the black oxide of iron (Fe_3O_4), which will be found in a crystalline state upon the surface of the metal. The decomposition is represented by the equation



$$\underset{\text{Water.}}{4H_2O} + Fe_3 = \underset{\text{Black oxide of iron.}}{Fe_3O_4} + H_8.$$

The weight of an atom of iron is believed to be 56 times that of an atom of hydrogen; hence the Fe_3 in the above equation represent 56 × 3, or 168 parts by weight of iron.

The process by which hydrogen is most commonly prepared consists in dissolving iron or zinc in a mixture of sulphuric acid and water.

Zinc is the most convenient metal to employ for the preparation of hydrogen in this way. It is used either in small fragments or cuttings, or as *granulated zinc*, prepared by melting it in a ladle and pouring it from a height of three or four feet into a pailful of water. The zinc is placed in the bottle (A, fig. 10), covered with water to the depth of two or three inches, and diluted sulphuric acid slowly poured in through the funnel tube (B) until a pretty brisk effervescence is observed. The hydrogen is unable to escape through the funnel tube, since the end of it is beneath the surface of the water, but it passes off through the bent tube (C), and is collected over water as usual, the first portion being rejected as containing air.

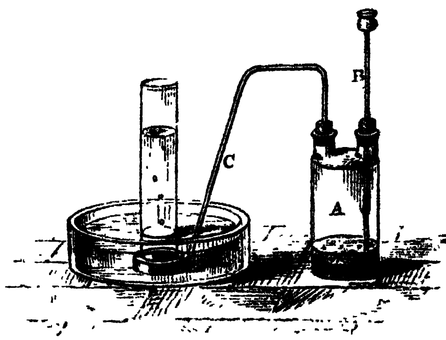
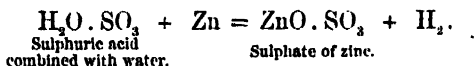


Fig. 10. – Preparation of hydrogen.

By evaporating the larger excess of water from the solution left in the bottle, crystals of sulphate of zinc (*white vitriol*) may be obtained.

It will be noticed that the liquid becomes very hot during the action of the acid upon the zinc, the heat being produced by the combination which is taking place. The black flakes which separate during the solution of the zinc consist of metallic lead, which is always present in the zinc of commerce, and much accelerates the evolution of hydrogen by causing galvanic action. Pure zinc placed in contact with diluted sulphuric acid evolves hydrogen very slowly.

The preparation of hydrogen by dissolving zinc in diluted sulphuric acid may be represented by the equation*



$$\underset{\text{Sulphuric acid combined with water.}}{H_2O\,.\,SO_3} + Zn = \underset{\text{Sulphate of zinc.}}{ZnO\,.\,SO_3} + H_2.$$

The symbol Zn here represents one atom of zinc, which is believed to be 65 times as heavy as the atom of hydrogen. An atom of zinc has here displaced two atoms of hydrogen, whereas it was found that an atom of potassium displaced only one atom of hydrogen, that is, 39 parts by weight of potassium are equivalent to 1 part of hydrogen.

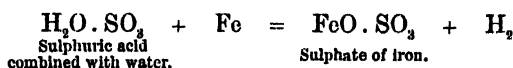
The atomic weight and equivalent weight of potassium, therefore, are represented by the same number, which is often expressed by saying that potassium is a *monatomic* element, *i.e.*, is exchangeable for one atom of hydrogen.

* In this equation the excess of water which must be added to dissolve the sulphate of zinc is not set down. Hydrogen could not be prepared according to the equation as it stands, because the sulphate of zinc would collect round the metal and prevent further action.

But since 65 parts of zinc displace 2 parts of hydrogen, the equivalent of zinc, or that quantity which is exchangeable for 1 part by weight of hydrogen, would be 32·5.

The atomic weight of zinc, therefore, is double its equivalent weight, or zinc is a *diatomic* element, *i.e.*, is exchangeable for two atoms of hydrogen. This is commonly expressed by writing the symbol of zinc thus—Zn″.

Iron might be used instead of zinc, and the solution when evaporated would then deposit crystals of *green vitriol* or *copperas* (sulphate of iron $FeO \cdot SO_3$), the action of iron upon water in the presence of sulphuric acid being represented by the equation



$$\underset{\text{Sulphuric acid combined with water.}}{H_2O \cdot SO_3} + Fe = \underset{\text{Sulphate of iron.}}{FeO \cdot SO_3} + H_2$$

which shows that one atom (56) of iron has taken the place of two atoms of hydrogen. 28 would then be the chemical equivalent of iron, and this metal is diatomic, like zinc.

11. *Physical properties of hydrogen.*—This gas is permanent, invisible, and inodorous when pure. The hydrogen obtained by the ordinary methods has a very disagreeable smell, caused by the presence of minute quantities of compounds of hydrogen with sulphur, arsenic, and carbon; but the gas prepared with pure zinc and sulphuric acid is quite free from smell. The most remarkable physical property of hydrogen is its lightness. It is the lightest of all kinds of matter, being about $\frac{1}{16}$ as heavy as air, and $\frac{1}{11162}$ as heavy as water.

The lightness of hydrogen may be demonstrated by many interesting experiments. Soap bubbles or small balloons (of *collodion* for example) will ascend very rapidly if inflated with hydrogen. A light beaker glass may be accurately weighed in a pair of scales; it may then be held with its mouth downwards, and hydrogen poured up into it from another vessel. If it be then replaced upon the scale-pan with its mouth downwards, it will be found very much lighter than before. Another form of the experiment is represented in fig. 11, where a light glass shade has been suspended from the balance and counterpoised, the equilibrium being, of course, at once disturbed when hydrogen is poured up into the shade. If a stoppered gas jar full of hydrogen be held with its mouth downwards, and a piece of smouldering brown paper held under it, the smoke, which would rise freely in the air, is quite unable to rise through the hydrogen, and remains at the mouth of the jar until the stopper is removed, when the hydrogen quickly rises and the smoke follows it.

12. The employment of hydrogen for filling balloons renders a knowledge of the relation between the weights of equal volumes of hydrogen and atmospheric air of great importance. The number expressing this relation is termed the *specific gravity* of hydrogen.

Definition.—The specific gravity of a gas or vapour is its weight as compared with that of an equal volume of some other gas, selected as a standard, at the same temperature and pressure.

If the weight of a given volume of purified and dried air be represented as unity, an equal volume of hydrogen, at the same temperature and pressure, would weigh 0·0692, which is expressed by saying that the specific gravity of hydrogen (air = 1) is 0·0692. In ascertaining the weights of definite volumes of gases, it is of the greatest importance that they should have some definite temperature and pressure, since the volume of a given weight of gas is augmented by increase of temperature and by

decrease in pressure. In England it is usual to state the weights of gases at the temperature of 60° on the Fahrenheit thermometer, and under a pressure of 30 inches of mercury in the barometer, these being regarded as the average conditions of the climate.



Fig. 11.

On the Continent the standard pressure is very nearly the same, being 760 millimetres of the barometric column, or 29·922 inches; but the standard temperature is that of melting ice, or 0° on the centigrade scale, corresponding to 32° F., a temperature to which gases may be reduced at will, by surrounding with melting ice the vessels in which they are collected for the purpose of being weighed.

One grain of hydrogen, at 60° F. and 30 inches Bar., measures 46·73 cubic inches.

Expressed on the Continental system, one gramme (15·43 grains) of hydrogen, at 0° C. and 760 mm. Bar., measures 11·19 litres (one litre = 61·024 cubic inches = 1·76 pints).

It is now easy to calculate how much zinc it would be necessary to dissolve in sulphuric acid in order to obtain any desired volume, say 100 cubic feet (172,800 cubic inches) of hydrogen. Referring to the equation for the preparation of hydrogen, $Zn + H_2O . SO_3 = H_2 + ZnO . SO_3$, and remembering that Zn represents 65 parts by weight of zinc, and H_2 2 parts by weight of hydrogen—

2 grs. H.		grs. Zn.		Cub. in.		
93·46 cub. in.	:	65	: :	172800	:	x (= 12018 grs. zinc).

13. It will be observed, in the experiment with the balance (fig. 11), that the gas gradually *falls* out of the jar, notwithstanding its lightness, and is replaced by air; so that, after a time, the equilibrium is restored. This is accounted for by a physical property belonging to all gases (and vapours) called *diffusibility*, which may be defined as *the tendency of the particles of a gas to separate as far as possible from each other.* If a jar of hydrogen were placed with its mouth downwards over a jar of air, this mutual repulsion among the particles of each

gas would cause it to *diffuse* itself equally throughout both jars, so that, eventually, as much hydrogen will be found in the lower jar as if it had been completely exhausted of air before the commencement of the experiment. This is often expressed by the statement that *one gas acts as a vacuum to another*, which is true as far as the ultimate result is concerned, though, of course, the time occupied by the passage of a gas into a *vacuum* would be far less than that required for its passage into another gas. Even if the two jars be connected only by a tube with the narrowest passage possible, the same result would be arrived at, but after a longer period.

This tendency of the particles of a gas to separate as far as possible from each other, or as it is sometimes called, the *mutual repulsion* of the particles of gases, is due to the constant movement of these particles; for although no appearance of motion can be seen, a little consideration will show that the particles of a gas are never at rest. It is well known that in a vessel containing a gas, the pressure of the gas is exerted equally in all directions upon the sides of the vessel; and if two vessels be filled with gases of different relative weights, the *pressure* may be the same in both, notwithstanding the difference in the actual *weights* of the gases. For example, if two jars of equal size be filled with hydrogen and oxygen, over the pneumatic trough, the pressure of each gas will equal that of the atmosphere, when the water within the jars has the same level as the water in the trough, although the actual weight of the oxygen is sixteen times that of the hydrogen.

The pressure of the gas upon the sides of the containing vessel is due to the constant motion of its particles, which causes them to strike upon the sides of the vessel with an amount of force which constitutes the pressure. Thus, in a gas having a pressure equal to that of the atmosphere, the particles of gas are delivering blows upon the sides of the containing vessel with a force amounting to about 15 lbs. upon every square inch of the surface. Since each particle of hydrogen is only $\frac{1}{16}$ of the weight of the particle of oxygen, it is evident that, in order to strike the sides of the vessel with the same force, the velocity of the hydrogen particles must be much greater than that of the oxygen particles. But if the hydrogen particles moved sixteen times as rapidly as the oxygen particles, not only would each hydrogen particle strike sixteen blows whilst each oxygen particle was striking one blow, but sixteen times as many hydrogen particles would deliver their blows in the same time, and we should have—

	Weight.		Velocity.		No. of strokes in same time.		Pressure.
Oxygen,	16	×	1	×	1	=	16
Hydrogen,	1	×	16	×	16	=	16 × 16.

If, however, the hydrogen particles move with four times the velocity of the oxygen particles, the pressures of the gases will be equal, thus—

	Weight.		Velocity.		No. of strokes in same time.		Pressure.
Oxygen,	16	×	1	×	1	=	16
Hydrogen,	1	×	4	×	4	=	16.

This affords an illustration of the law that the *rates of diffusion of the gases are inversely as the square roots of their relative weights.*

Rate of Diffusion of Hydrogen, : Rate of Diffusion of Oxygen, : : $\sqrt{16}$: $\sqrt{1}$.

It has been calculated that the actual velocity or *rate of translation* of the particles of hydrogen amounts to 6050 feet per second.

When a jar of hydrogen, having its mouth turned upwards, is open to the air, the rapid escape of the hydrogen is due, firstly, to its displacement, in consequence of the heavier air falling into the jar; and, secondly, to the rapid motion or diffusion of the particles of the hydrogen, which projects them out of the mouth of the vessel. It is found that the escape due to the first of these causes may be prevented by clos-

ing the mouth of the vessel with a plate of dry plaster of Paris, or of certain other materials having very minute pores; but this does not prevent the escape of the hydrogen by diffusion, and therefore permits the rate of diffusion to be measured.

The *diffusion tube* (fig. 12) employed for this purpose is a glass tube (A) closed at one end by a plate of plaster of Paris (B). If this tube be filled with hydrogen,* and its open end immersed in coloured water, the water will be observed to rise rapidly in the tube, on account of the rapid escape of the hydrogen through the pores of the plaster. The external air, of course, passes into the tube through the pores at the same time, but much less rapidly than the hydrogen passes out, so that the ascent of the column of water (C) marks the difference between the volume of hydrogen which passes out, and that of air which passes into the tube in a given time, and allows a measurement to be made of the *rate of diffusion;* that is, of the velocity with which the gas issues on account of the repulsion among its particles, as compared with the velocity with which the air enters, this velocity being always taken as unity.† To determine the rate of diffusion, it is of course necessary to maintain the water at the same level within and without the diffusion tube, so as to exclude the influence of pressure.

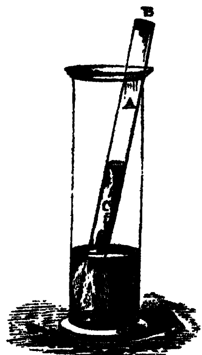


Fig. 12.

To prove that the ascent of the hydrogen due to its lightness is not instrumental in drawing up the water in the diffusion tube, the experiment may be made as in fig. 13, where the plate of plaster (*o*) is turned downwards, so that the diffusion is made to take place in opposition to the action of gravity. This tube is filled by passing hydrogen in through the tube (*s*), and allowing the air to escape through (*t*), which is afterwards closed by a cork. The plaster of Paris (*o*) is tied over with caoutchouc whilst the tube is filled.

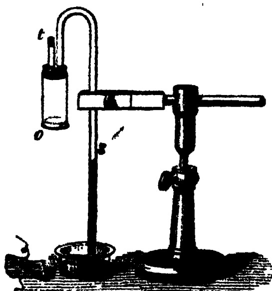


Fig. 13.—Diffusion tube.

Since the relation between the weights of equal volumes of hydrogen and air is that of 0·069 : 1, the rates of diffusion will be as 1 : $\sqrt{0{\cdot}069}$— that is, hydrogen will diffuse about 3·8 times as rapidly as atmospheric air, or 3·8 measures of hydrogen will pass out of the diffusion tube whilst one measure of air is passing in through the plaster. In a similar manner hydrogen would escape through minute openings with nearly four times the velocity of oxygen; and laboratory experience shows that a cracked jar, or a bottle with a badly fitting stopper, may often be used to retain oxygen, but not hydrogen.

A very striking illustration of the high rate of diffusion of hydrogen is arranged as represented in fig. 14. A is a cylinder of porous earthenware (such as are employed in galvanic batteries) closed at one end, and furnished at the other with a perforated bung, through which passes a glass tube B, about three feet long, and half an inch in diameter. The bung is made air-tight by coating it with sealing wax dissolved in spirit of wine. This tube being supported so that its lower end dips about an inch below the surface of water, a jar of hydrogen is held over the porous cylinder, when the self-repulsion of the particles of the gas is manifested by their being forced (not only out of the mouth of the jar C, which is open at the bottom, but also) through the pores of the earthenware jar, the air from which is violently driven out, as if by blowing, through the tube, and is seen bubbling up rapidly through the water. When the air has ceased to bubble out, and a large volume of hydrogen has entered the porous jar, the bell-jar C is removed, when the hydrogen escapes so rapidly through the pores, that a column of twenty or thirty inches of water is drawn rapidly up the tube B. If the greatest height to which the water ascends be marked, and when it has returned to its former level, a jar of coal-

* This tube must be filled by displacement (see fig. 18), in order not to wet the plaster. A piece of sheet caoutchouc may be tied over the plaster of Paris, so that diffusion may not commence until it is removed.

† Air being a mixture of nitrogen and oxygen, its rate of diffusion is intermediate between the rates of those gases; however, since the proportions of the gases are very nearly constant, no error of any magnitude arises.

gas be held over the porous cylinder, it will be found that the above phenomena are manifested in a much lower degree, showing that coal-gas, being heavier than hydrogen, does not pass nearly so rapidly through the pores of the earthenware as hydrogen does.

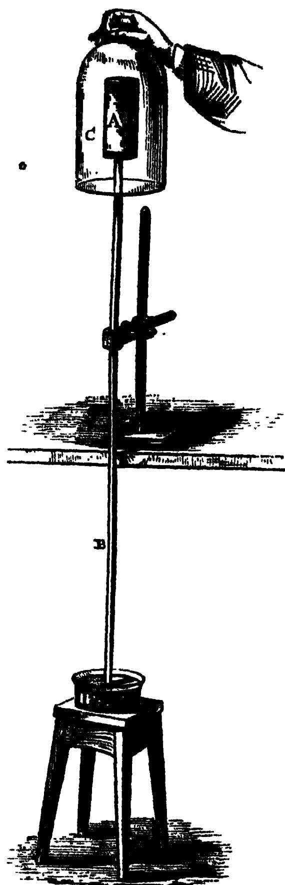


Fig. 14.

The great difference in the rates of diffusion of hydrogen and oxygen may be easily shown by the arrangement represented in fig. 15. A, is a jar filled with a mixture of two volumes of oxygen with one volume of hydrogen, communicating through the stop-cock and flexible tube with the glass tube B, which is fitted through a perforated cork in the bowl of the common tobacco pipe C, the sealing-waxed end of which dips under water in the trough D. By opening the stop-cock and pressing the jar down in the water, the mixed gases may be forced rapidly through the pipe, and if a small cylinder (E) be filled with them, the mixture will be found to detonate violently on the approach of a flame. But if the gas be made to pass very slowly through the pipe (at the rate of about a cubic inch per minute), the hydrogen will diffuse through the pores of the pipe so much faster than the oxygen, that the gas collected in the cylinder will contain so little hydrogen as to be no longer explosive, and to exhibit the property of oxygen to rekindle a partly extinguished match.

If two jars of the same size, one made of glass, and the other of porous earthenware, be filled with the explosive mixture by holding them over the stop-cock of the jar A, and be then closed with glass plates and set aside for a few seconds, it will be found that the gas in the earthen jar will rekindle a spark on a match, whilst that in the glass jar will explode.

14. *Chemical properties of hydrogen.*—The most conspicuous chemical property of hydrogen is its disposition to burn in air when raised to a moderately high temperature, entering into combination with the oxygen of the air to form water. The formation of water during the combustion of hydrogen gave rise to its name (ὕδωρ, water).

On introducing a taper into an inverted jar of hydrogen (fig. 16), the flame of the taper will be extinguished, but the hydrogen will burn with a pale flame at the mouth of the jar, and the taper may be rekindled at its flame by slowly withdrawing it.

The lightness and combustibility of hydrogen may be illustrated simultaneously by some interesting experiments. If two equal gas cylinders be filled with hydrogen, and held with their mouths respectively upwards and downwards, it will be found, on testing each with a taper after the same interval, that the hydrogen has entirely escaped from the cylinder held with its mouth upwards, whilst the other still remains nearly filled with the gas.

The hydrogen may be scooped out of the jar A (fig. 17) with the small cylinder B attached to a handle. On removing B, and applying a taper to it, the gas will take fire.

A cylinder may be filled with hydrogen by displacement of air (fig. 18), if the tube from the hydrogen bottle be passed up into it.

If such a dry cylinder of hydrogen be kindled whilst held with its mouth downwards, the formation of water during the combustion of the hydrogen will be indicated by the deposition of dew upon the sides of the cylinder.

By softening a piece of glass tube in the flame of a spirit-lamp, drawing it out and filing it across in the narrowest part (fig. 19), a jet can be made from which the hydrogen may be burnt. This jet may be fitted by a perforated cork to any common bottle for containing the zinc and sulphuric acid (fig. 20).

The hydrogen must be allowed to escape for some minutes before applying a light, because it forms an explosive mixture with the air contained in the bottle. This

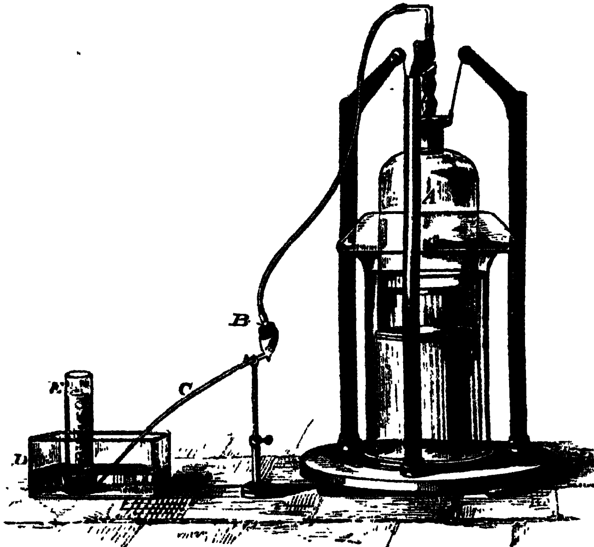


Fig. 15.—Separation of hydrogen and oxygen by atmolysis.*

may be proved, without risk, by placing a little granulated zinc in a soda-water bottle, pouring upon it some diluted sulphuric acid, and quickly inserting a perforated



Fig. 16.

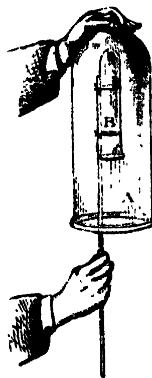


Fig. 17.

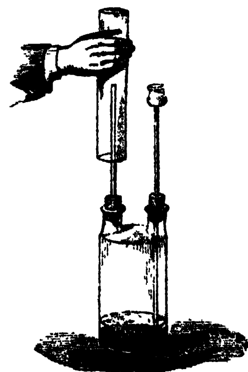


Fig. 18.

cork, carrying a piece of glass tube about three inches long, and one-eighth of an inch wide. If this tube be immediately applied to a flame, the mixture of air and hydrogen will explode, and the cork and tube will be projected to a considerable distance.

By inverting a small test-tube over the jet in fig. 20, a specimen of the hydrogen may be collected, and may be kindled, to see if it burns quietly, before lighting the jet.



Fig. 19.

* This term has been applied to the separation of gases by diffusion; ἀτμός, *vapour*—λύω, to loosen.

A dry glass, held over the flame, will collect a considerable quantity of water, formed by the combustion of the hydrogen.

The combustion of hydrogen produces a greater heating effect than that of an equal weight of any other combustible body. It has been determined that 1 gr. of hydrogen, in the act of combining with 8 grs. of oxygen, produces enough heat to raise 62,031 grs. of water from 32° F. to 33° F. (or 34,462 grs. from 0° C. to 1° C.) The temperature of the hydrogen flame is higher than that of any other single flame with which we are acquainted. Notwithstanding its high temperature, the flame of hydrogen is almost devoid of illuminating power, on account of the absence of solid particles.

15. If a taper be held several inches above a cylinder of hydrogen, standing with its mouth upwards, the gas will be kindled with a loud explosion, because an explosive mixture of hydrogen and air is formed in and around the mouth of the cylinder.

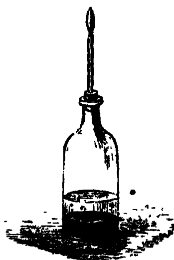


Fig. 20.



Fig. 21.

If a stoppered gas jar (fig. 21) be filled with hydrogen, and supported upon three blocks, it will be found, if the hydrogen be kindled at the neck of the jar, that it will burn quietly until air has entered from below in sufficient proportion to form an explosive mixture, which will then explode with a loud report.

The same experiment may be tried on a smaller scale, with the two-necked copper vessel (fig. 22), the lower aperture being opened some few seconds after the hydrogen has been kindled at the upper one.



Fig. 22.

The explosion of the mixture of hydrogen and air is due to the sudden expansion caused by the heat generated in the combination of the hydrogen with the oxygen throughout the mixture. After the explosion of the mixture of hydrogen and air (oxygen and nitrogen), the substances present are steam (resulting from the combination of the hydrogen and oxygen) and nitrogen, which are expanded by the heat developed in the combination to a volume far greater than the vessel can contain, so that a portion of the gas and vapour issues very suddenly into the air around, the collision with which produces the report.

If pure oxygen be substituted for air, the explosion will be more violent, because the mixture is not diluted with the inactive nitrogen. The further study of this subject must be preceded by that of oxygen.

OXYGEN.

O = 16 parts by weight = 1 vol. 16 grs. = 46·7 cub. in. at 60° F. and 30″ Bar. 16 grammes = 11·2 litres at 0° C. and 760 mm. Bar.

16. Oxygen is the most abundant of the elementary substances. It constitutes about one-fifth (by volume) of atmospheric air, where it is merely *mixed*, not combined, with the nitrogen, which composes the bulk of the remainder. Water contains eight-ninths (by weight) of oxygen; whilst silica and alumina, which compose the greater part of the solid earth (as far as we know it), contain about half their weight of oxygen.

Before inquiring which of these sources will most conveniently furnish pure oxygen, it will be desirable for the student to acquire some knowledge of the properties of this element, and of the chemical relations which it bears to other elementary bodies, for without such knowledge it will be found very difficult to understand the processes by which oxygen is procured.

17. *Physical properties of Oxygen.*—From the fact of its occurring in an uncombined state in the atmosphere, it will be inferred that oxygen is perfectly invisible, and without odour. It is a *permanent gas*, having resisted all attempts to reduce it to a liquid or solid state. Oxygen is a little more than one-tenth heavier than air, which is expressed in the statement that its specific gravity is 1·1057.

In the study of theoretical chemistry, it is expedient to select hydrogen instead of air as the standard with which the specific gravities of gases are compared; for since the atomic weights are also referred to hydrogen as the unit, and the atomic weights represent the weights of equal volumes, the members expressing the *atomic weights of the elementary gases are identical with their specific gravities* ($H = I$). Thus, the specific gravity of oxygen (H = I) is 16. It will be found convenient to remember that *the specific gravity of a gas or vapour is the weight of one volume.*

18. *Chemical properties of Oxygen.*—This element is remarkable for the wide range of its chemical attraction for other elementary bodies, with all of which, except one, it is capable of entering into combination. *Fluorine is the only element which is not known to unite with oxygen.*

With nearly all the elements oxygen combines in a direct manner; that is, without the intervention of any third substance.

There are only *seven elements* (among those of practical importance) *which do not unite in a direct manner with oxygen*, viz., *chlorine, bromine, iodine, fluorine, gold, silver, platinum.*

(Definition.—The compounds of oxygen with other elements are called *Oxides.*)

The act of combination with oxygen, or *oxidation*, like all other acts of chemical combination, is attended with the development of heat.* When the heat thus produced is sufficient to render the particles of matter luminous, the act of combination is styled combustion.

* Though this heat is not always perceptible by the thermometer or by the senses. Thus, when chalk is dissolved in an acid, no heat is perceived, because all the heat attending the union of the lime with the acid is consumed in converting the carbonic acid from the solid chalk into a gas. To explain the manifestation of heat in the act of chemical combination falls within the province of the physicist rather than of the chemist. Modern writers attribute it to the motion of the molecules which compose the combining masses.

(DEFINITION.—*Combustion* is chemical combination attended with heat and light.)

19. *Phosphorus, the only non-metal which combines with oxygen at the ordinary temperature,* affords a good illustration of these propositions. This element, a solid at the ordinary temperature, is preserved in bottles filled with water, on account of the readiness with which the oxygen of the air combines with it. If a small piece of phosphorus be dried by gentle pressure between blotting paper, and exposed to the air, its particles begin to combine at once with oxygen, and the heat thus developed slightly raises the temperature of the mass.

Now, *heat generally encourages chemical union,* so that the effect of this rise of temperature is to induce a more extensive combination of the phosphorus with the oxygen, causing a greater development of heat in a given time, until the temperature is sufficient to render the particles brilliantly luminous, and a true case of combustion results—the combination of the phosphorus with oxygen, attended with production of heat and light.

(DEFINITION.—*Combustion in air* is the chemical combination of the elements of the combustible with the oxygen of the air, attended with development of heat and light.)

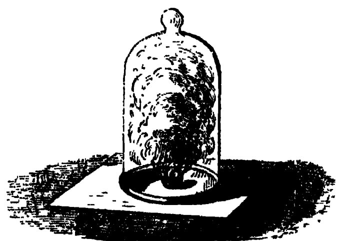


Fig. 23.

If a dry glass (fig. 23) be placed over the burning phosphorus, the thick white smoke which proceeds from it may be collected in the form of snowy flakes. These flakes are commonly termed *anhydrous phosphoric acid,** and are composed of 80 parts by weight of oxygen, and 62 parts of phosphorus (P_2O_5).

If the white flakes are exposed to the air for a short time, they attract moisture and become little drops, which have a very sour or *acid* taste. It was mentioned at page 10 that all substances which have such a taste have been found also to be capable of changing the blue colour of *litmus*† to red, whence the chemist is in the habit of employing paper dyed with blue litmus for the recognition of an acid. It must be remembered, however, that there are some acids which, not being dissolved by water, have neither a sour taste nor the power of reddening litmus, so that, in exact research, another mode of defining the acid character of a substance is employed. Ordinary sand is known to chemists as *silicic acid,* but, of course, does not answer to either of the above tests.

For the exact definition of an acid see page 25.

During the slow combination of phosphorus with the oxygen of the air, before actual combustion commences, only 48 parts of oxygen unite with 62 parts of phosphorus, forming the substance called anhydrous *phosphorous acid* (P_2O_3).

(DEFINITION.—*The endings -ous and -ic* distinguish between two compounds formed by oxygen with the same element; *-ous* implying the smaller proportion of oxygen.)

* *Anhydrous,* or without water, from *αν,* negative, and *ὕδωρ,* water.

† A colouring matter, prepared from a lichen, *Roccella tinctoria;* the cause of the change of colour will be more easily understood hereafter.

Unless the temperature of the air be rather high, the fragment of phosphorus will not take fire spontaneously, but its combustion may always be ensured by exposing a larger surface to the action of the air. As a general rule, *a fine state of division favours chemical combination*, because the attractive force inducing combination operates only between substances in actual contact; and the smaller the size of the particles, the more completely will this condition be fulfilled.

Thus, if a small fragment of dry phosphorus be placed in a test-tube, and dissolved in a little *bisulphide of carbon*, the solution, when poured upon blotting paper (fig. 24), will part with the solvent by evaporation, leaving the phosphorus in a very finely divided state upon the surface of the paper, where it is so rapidly acted on by the oxygen of the air that it bursts spontaneously into a blaze.

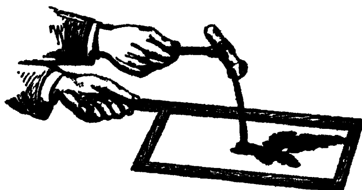


Fig. 24.

Though the light emitted by phosphorus burning in air is very brilliant, it is greatly increased when pure oxygen is employed; for since the nitrogen with which the oxygen in air is mixed takes no part in the act of combustion, it impedes and moderates the action of the oxygen. Each volume of the latter gas is mixed, in air, with four volumes of nitrogen, so that we may suppose five times as many particles of oxygen to come into contact, in a given time, with the particles of the phosphorus immersed in the pure gas, which will account for the great augmentation of the temperature and light of the burning mass.

To demonstrate the brilliant combustion of phosphorus in oxygen, a piece not larger than a good-sized pea is placed in a little copper or iron cup upon an iron stand (fig. 25), and kindled by being touched with a hot wire (for even in pure oxygen spontaneous combustion cannot be ensured). The globe, having been previously filled with oxygen, and kept in a plate containing a little water, is placed over the burning phosphorus.*

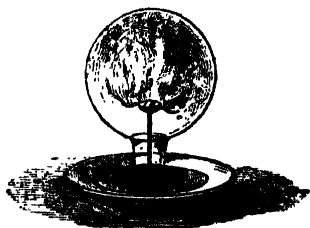


Fig. 25.—Phosphorus burning in oxygen.

It will be observed that the same white clouds of phosphoric acid are formed, whether phosphorus is burnt in oxygen or in air, exemplifying the fact that *a substance will combine with the same proportion of oxygen, whether its combustion be effected in pure oxygen or in atmospheric air.* The apparent increase of heat is due to the combustion of a greater weight of phosphorus in a given time and space. The total heating effect produced by the combustion of a given weight of phosphorus is the same whether air or pure oxygen be employed.

20. Sulphur (*brimstone*) affords an example of a non-metallic element which will not enter into combination with oxygen until its temperature has been raised very considerably. When sulphur is heated in air, it soon melts; and as soon as its temperature reaches 500° F. it takes fire, burning with a pale blue flame. If the burning sulphur be plunged into a jar of oxygen, the blue light will become very brilliant, but the same

* This globe should be of thin, well-annealed glass, and is sure to be broken if too large a piece of phosphorus be employed.

act of combination takes place—32 parts by weight of oxygen uniting with 32 parts of sulphur to form *sulphurous acid* gas (SO_2), which may be recognised in the jar by the well-known suffocating smell of brimstone matches.

The experiment is most conveniently performed by heating the sulphur in a *deflagrating spoon* (A, fig. 26), which is then plunged into the jar of oxygen, its collar (B) resting upon the neck of the jar, which stands in a plate containing a little water. The water absorbs a part of the sulphurous acid gas, and will be found capable of strongly reddening litmus paper. It is possible to produce, though not by simple combustion, a compound of sulphur with half as much more oxygen (SO_3, anhydrous sulphuric acid), showing that *a substance does not always take up its full share of oxygen when burnt.*

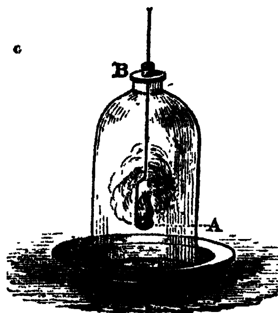


Fig. 26.—Sulphur burning in oxygen.

The luminosity of the flame of sulphur is far inferior to that of phosphorus, because, in the former case, there are no minute solid particles in the flame corresponding to those of the phosphoric acid produced in the combustion of phosphorus, and *no flame can emit a brilliant light unless it contains solid matter heated to incandescence.*

21. Carbon, also a non-metallic element, requires the application of a higher temperature than sulphur to induce it to enter into direct union with oxygen; indeed, perfectly pure carbon appears to require a heat approaching whiteness to produce this effect. But charcoal (the carbon in which is associated with not inconsiderable proportions of hydrogen and oxygen) begins to burn in air at a much lower temperature; and if a piece of wood charcoal, with a single spot heated to redness, be lowered into a jar of oxygen, the adjacent particles will soon be raised to the combining temperature, and the whole mass will glow intensely, 32 parts by weight of oxygen uniting with 12 parts of carbon to form *carbonic acid* (CO_2) gas, which will redden a piece of moistened blue litmus paper suspended in the jar, though much more feebly than either sulphurous or phosphoric acid, because it is a much weaker acid. It should be remembered that *carbon is an essential constituent of all ordinary fuel, and carbonic acid is always produced by its combustion.*

It will be noticed that the combustion of the charcoal is scarcely attended with flame; and when pure carbon (diamond, for example) is employed, no flame whatever is produced in its combustion, because carbon is not convertible into vapour, and all *flame is vapour or gas in the act of combustion;* hence, *only those substances burn with flame which are capable of yielding combustible gases or vapours.*

22. The three examples of sulphur, phosphorus, and carbon sufficiently illustrate the tendency of non-metals to form acids by union with oxygen, which originally led to the adoption of its name, derived from ὀξύς acid, and γεννάω, I produce. *All the non-metallic elements, except hydrogen and fluorine, are capable of forming acids by their union with oxygen.*

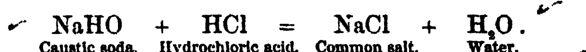
The circumstance that only those acids which can be dissolved by water have any action upon litmus, and that some of these have a very feeble effect, renders it necessary to fix some other criterion by which an acid may be invariably recognised. Such a criterion is found in the original idea of an acid, as a substance neutralising an alkali. In the case of some acids, such as sulphuric, it is easy to exhibit the neutralising power; but with others, such as carbonic and silicic, it is not so easy to ascertain that neutralisation has taken place, because the alkali is only partly neutralised. In practice, therefore, the following definition will be found more convenient:—

Definition of an Acid.—A compound body which evolves water by its action upon pure caustic potash or soda.

For example—



$$2\,KHO + CO_2 = K_2O.CO_2 + H_2O$$
Caustic potash. Carbonic acid. Carbonate of potash. Water.



$$NaHO + HCl = NaCl + H_2O.$$
Caustic soda. Hydrochloric acid. Common salt. Water.

23. The metals, as a class, exhibit a greater disposition to unite directly with oxygen, though few of them will do so in their ordinary condition, and at the ordinary temperature. Several metals, such as iron and lead, are superficially oxidised when exposed to air under ordinary conditions, but this would not be the case unless the air contained water and carbonic acid, which favour the oxidation in a very decided manner. Among the metals which are of importance in practice, five only are oxidised by exposure to dry air at the ordinary temperature, viz., potassium, sodium, barium, strontium, and calcium, the attraction of these metals for oxygen being so powerful that they must be kept under petroleum, or some similar liquid free from oxygen. On the other hand, three of the common metals, silver, gold, and platinum, have so little attraction for oxygen that they cannot be induced to unite with it directly, even at high temperatures.

If a lump of sodium be cut across with a knife, the fresh surfaces will exhibit a splendid lustre, but will very speedily tarnish by combining with oxygen from the air, which gives rise to a coating of *oxide of sodium* or *soda*, and this to some extent protects the metal beneath from oxidation. The freshly cut sodium shines, in the dark, like phosphorus. Even when the attraction of the sodium for oxygen is increased by the application of heat, it is long before the mass of sodium is oxidised throughout, unless the temperature be sufficiently high to convert a portion of the sodium into vapour, which bursts through the crust of soda, and burns with a yellow flame. If the spoon containing the sodium (see fig. 26) be now plunged into a jar of oxygen, the yellow flame will be far more brilliant.

Sixteen parts by weight of oxygen here combine with 46 parts of sodium to form soda (Na_2O), which remains in the spoon in a fused state. When the spoon is cool, it may be placed in water, which will dissolve the soda, converting it into caustic soda.



$$Na_2O + H_2O = 2NaHO.$$
Soda. Water Caustic soda.

24. Zinc will serve as an example of a metal which has no disposition

to enter into combination with oxygen at the ordinary temperature,* but which is induced to unite with it by a very moderate heat. If a little zinc (*spelter*) be melted in a ladle or crucible, and stirred about with an iron rod, it burns with a beautiful greenish flame produced by the union of the vapour of zinc with the oxygen of the air. But the combustion is far more brilliant if a piece of zinc-foil be made into a tassel (fig. 27), gently warmed at the end, dipped into a little flowers of sulphur, kindled, and let down into a jar of oxygen, when the flame of the burning sulphur will ignite the zinc, which burns with great brilliancy. On withdrawing what remains of the tassel after the combustion is over, it will be found to consist of a friable† mass, which has a fine yellow colour while hot, and becomes white as it cools. This is the *oxide of zinc* (ZnO), formed by the union of 16 parts by weight of oxygen with 65 parts of zinc.

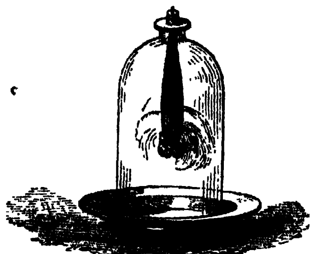


Fig. 27.—Zinc burning in oxygen.

The oxide of zinc does not possess the properties of an acid or an alkali, but belongs to another class of compounds termed *bases*, which are not soluble in water as the alkalies are, but, like them, are capable of neutralising, either partly or entirely, the acids. Thus, if the oxide of zinc were added to diluted sulphuric acid as long as the acid would dissolve it, the well-known corrosive properties of the acid would be destroyed, although it would still retain the power of reddening blue litmus, and the solution would now contain a new substance, or salt, called *sulphate of zinc* ($ZnO.SO_3$).

(Definition.—A *base* is a compound body which is capable of neutralising an acid, either partly or entirely.)

It will be observed that an alkali is only a particular species of base, and might be defined as a base which is very soluble in water.

(Definition.—A *salt* is a compound body containing an acid in combination with a base, or a metal in combination with a *salt-radical*.‡ *Examples.*—Carbonate of soda ($Na_2O.CO_2$), composed of carbonic acid (CO_2) and soda (Na_2O); Chloride of sodium (NaCl), composed of the metal sodium and the salt-radical chlorine.)

(Definition.—A *salt-radical* or *halogen* is a substance which forms an acid when combined with hydrogen. *Examples.*—Chlorine, which forms hydrochloric acid (HCl); Cyanogen (CN), which forms hydrocyanic acid (HCN).)

25. Iron, in its ordinary form, like zinc, is not oxidised by *dry* air or oxygen at the ordinary temperature; but if it be heated even to only 500° F. a film of oxide of iron forms upon its surface, and as the heat is increased the thickness of the film increases, until eventually it becomes so thick that it can be detached by hammering the surface, as may be seen in a smith's forge. If an iron rod as thick as the little finger be heated to whiteness at the extremity, and held before the nozzle of a powerful bellows, it will burn brilliantly, throwing off sparks and dropping melted

* Unless water and carbonic acid be present, as in common air.

† *Friable*, easily crumbled or disintegrated.

‡ Salts of this description are termed *haloid salts*, because they belong to the same class as sea-salt (NaCl), from ἅλς, the sea.

oxide of iron. If a stream of oxygen be substituted for air, the combustion is of the most brilliant description. A watch-spring (iron combined with about 1 per cent. of carbon) may be easily made to burn in oxygen by heating it in a flame till its elasticity is destroyed, and coiling it into a spiral (A, fig. 28), one end of which is fixed, by means of a cork, in the deflagrating collar B; if the other end be filed thin and clean, dipped into a little sulphur, kindled, and immersed in a jar of oxygen (C) standing in a plate of water, the burning sulphur will raise the iron to the point of combustion, and the spring will be converted into molten drops of oxide.

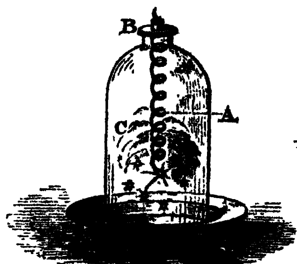


Fig. 28.—Watch-spring burning in oxygen.

The black oxide of iron formed in all these cases is really a combination of two distinct oxides of iron, one of which contains 16 parts by weight of oxygen and 56 parts of iron, and would be written FeO, whilst the other contains 48 parts of oxygen and 112 parts of iron, expressed by the formula Fe_2O_3. To distinguish them, the former is usually called *protoxide* of iron (πρῶτος, first), and the latter *sesquioxide* (in allusion to the ratio of one and a half to one between the oxygen and the metal).* The sesquioxide of iron combined with water constitutes ordinary rust.

The black oxide usually contains one combining weight of each oxide, so that it would be written $FeO.Fe_2O_3$, or Fe_3O_4. It is powerfully attracted by the magnet, and is often called magnetic oxide of iron. The abundant magnetic ore of iron, of which the *loadstone* is a variety, has a similar composition.

Iron in a very fine state of division will take fire spontaneously in air as certainly as phosphorus. *Pyrophoric* iron can be obtained (by a process to be described hereafter) as a black powder, which must be preserved in sealed tubes. When the tube is opened, and its contents thrown into the air, oxidation takes place, and is attended with a vivid glow. In this case the red sesquioxide of iron is produced instead of the black oxide.

Both these oxides of iron are capable of neutralising, or partially neutralising, acids, and are therefore basic oxides or bases, like the oxides of zinc and sodium obtained in previous experiments. So general is the disposition of metals to form oxides of this class, that it may be regarded as one of the distinguishing features of a metal, for no non-metal ever forms a base with oxygen.

(Definition.—A *metal* is an element capable of forming a base† by combining with oxygen, or salt by combining with a salt-radical.)

Many metals are capable also of forming acids with oxygen; thus, tin forms stannic acid (SnO_2), antimony forms antimonic acid (Sb_2O_5), and it is always found that the acid oxide of a metal contains a larger proportion of oxygen than any of the other oxides which the metal may happen to form.

26. There is a third class of oxides, termed the *indifferent oxides*, because they are neither acids nor bases; such oxides may be formed either

* The terms ferrous and ferric oxide are now very often substituted for protoxide and sesquioxide of iron.

† The metal tungsten appears at present to be an exception to this rule, no well-defined basic oxide of this metal being known.

by non-metals or metals; thus water (H_2O), the oxide of hydrogen, is an indifferent oxide, and the black oxide or binoxide of manganese (MnO_2) is an example of an indifferent metallic oxide.

27. *Preparation of Oxygen.*—For almost all the useful arts in which uncombined oxygen is required, the diluted gas contained in atmospheric air is sufficient, since the nitrogen mixed with it does not interfere with its action.

From atmospheric air pure oxygen was first obtained by Lavoisier towards the end of the last century. His process is far too tedious to be employed as a general method of preparing oxygen, but it affords a very good example of the relation of heat to chemical attraction. Some mercury was poured into a glass flask with a long narrow neck, which was placed in a sand-bath, so that its temperature might be constantly maintained at about 660° F. for several weeks. The mercury boiled, and a portion of it was converted into vapour, which condensed in the neck of the flask and ran back again. Eventually the mercury was converted into a red powder, having combined with the oxygen of the air (or undergone *oxidation*) to form the *red oxide of mercury*. The nitrogen of the air does not enter into combination with the mercury.

By heating this oxide of mercury to a temperature approaching a red heat (about 1000° F.) it is decomposed into mercury and oxygen gas ($HgO = Hg + O$).

It is very generally found, as in this instance, that heat of moderate intensity will favour the operation of chemical attraction, whilst a more intense heat will annul it.

For the purpose of experimental demonstration, the decomposition of the oxide of mercury may be conveniently effected in the apparatus represented by fig. 29, where the oxide is placed in the German glass tube A, and heated by the Bunsen's

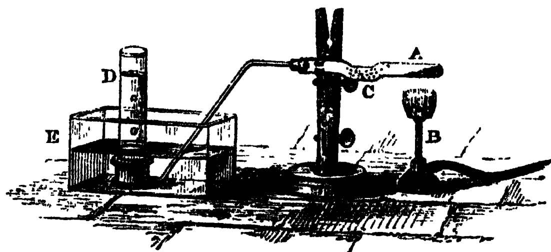


Fig. 29.—Preparation of oxygen from oxide of mercury.

gas-burner B, the metallic mercury being condensed in the bend C, and the oxygen gas collected in the gas cylinder D, filled with water, and standing upon the bee-hive shelf of the *pneumatic trough* E. It may be identified by its property of kindling into flame the spark left at the end of a wooden match. If the heat be continued for a sufficient length of time, the whole of the oxide of mercury will disappear, being resolved into its elements. In technical language, the mercury is said to be *reduced*.

Upon the first application of heat, the red oxide suffers a physical change, in consequence of which it becomes black; but its red colour returns again if it be allowed to cool.

A much cheaper process for obtaining unmixed oxygen from the air is now employed upon the large scale. It depends upon the principle that the oxides of manganese, when heated in contact with alkalies and air,

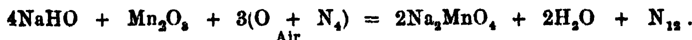
are capable of absorbing the oxygen from the air, and of subsequently giving it up again if heated in a current of steam.

To illustrate this process, about four ounces of dry manganate of soda (which may be purchased cheaply in a crude state) are introduced into a porcelain tube (*t*, fig. 30) fixed in a furnace. One end of the tube is connected with a two branched glass tube, so that either a current of air may be passed through it by the tube *a*, or a current of steam from the flask *w*. On heating the manganate of soda in the tube to dull redness, and passing the steam over it, oxygen is evolved, and may be collected in the jar *o*.



$$\underset{\text{Manganate of soda.}}{2Na_2MnO_4} + 2H_2O = \underset{\text{Caustic soda.}}{4NaHO} + \underset{\text{Sesquioxide of manganese.}}{Mn_2O_3} + O_3.$$

If the current of steam be discontinued, and air be slowly passed through the tube *a*, the oxygen of the air will be absorbed, and its nitrogen may be collected in the jar *n*.



$$4NaHO + Mn_2O_3 + 3\underset{\text{Air.}}{(O + N_4)} = 2Na_2MnO_4 + 2H_2O + N_{12}.$$

If the proper temperature be employed, the stream of gas issuing from the tube may be constantly kept up, and may be made to consist of oxygen or nitrogen accordingly as steam or air is passed through the tube. The current of air is regulated by the nipper-tap *c*.

The gas-furnace represented in fig. 30 consists of a row of twelve Bunsen burners, each having a stop-cock by which the flame is regulated. The horizontal pipe *b*, from which they spring, is capable of being raised or lowered at pleasure. The porcelain tube *t* is laid in a semi-cylindrical trough made of stout iron rods, and filled with pieces of pumice-stone or fire-brick. Above this is placed a corresponding trough, so that the tube is entirely surrounded by glowing material.* The heat must be applied gradually to avoid splitting the tube.

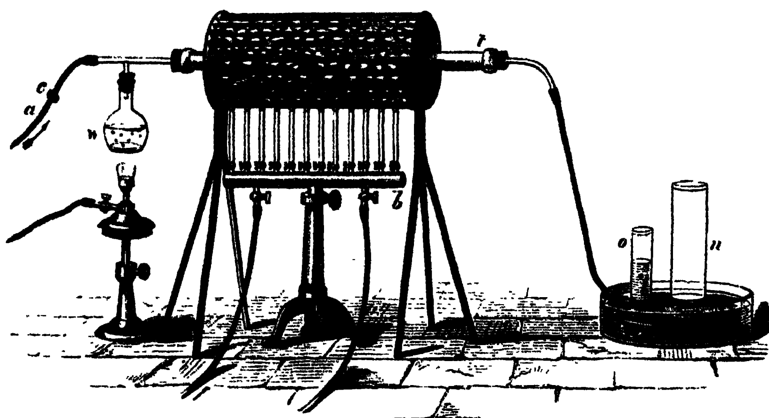


Fig. 30 – Extraction of oxygen from air.

28. The only other natural source from which it has been found convenient to prepare pure oxygen is a black mineral composed of manganese and oxygen. It is found in some parts of England, but much more abundantly in Germany and Spain, whence it is imported for the use of the bleacher and glass-maker. Its commercial name is *manganese*, but it

* This burner, as well as the burner described at page 8, was constructed for me by Mr Rowley, of the Royal Military Academy, Woolwich, whose readiness in perceiving the intention of an apparatus, and in improving upon the original idea as the work proceeds, renders his co-operation in arranging experimental illustrations of the greatest service to me.

is known to chemists as *binoxide of manganese* (MnO_2), and to mineralogists by several names designating different varieties. The most significant of these names is *pyrolusite,* referring to the facility with which it may be decomposed by heat (πυρ, fire, and λυω, to loosen).

One of the cheapest methods of preparing oxygen consists in heating small fragments of this black oxide of manganese in an iron retort, placed in a good fire, the gas being collected in jars filled with water, and standing upon the shelf of the pneumatic trough, or in a gas-holder or gas-bag, if larger quantities are required.

The attraction existing between manganese and oxygen is too powerful to allow the metal to part with the whole of its oxygen when heated, so that only one-third of the oxygen is given off in the form of gas, a brown oxide of manganese being left in the retort.*

29. By far the most convenient source of oxygen, for general use in the laboratory, is the artificial salt called *chlorate of potash,* which is largely manufactured for fireworks, percussion-cap composition, &c. If a few crystals of this salt be heated in a test-tube over a spirit-lamp (fig. 31), it soon melts to a clear liquid, which presently begins to boil from the disengagement of bubbles of oxygen, easily recognised by introducing a match with a spark at the end into the upper part of the tube. If the action of heat be continued until no more oxygen is given off, the residue in the tube will be the salt termed chloride of potassium.†

Fig. 31.

$$\underset{\text{Chlorate of potash.}}{KClO_3} = \underset{\text{Chloride of potassium.}}{KCl} + O_3.$$

To ascertain what quantity of oxygen would be furnished by a given weight of chlorate of potash, the combining weights must be brought into use. Referring to the table of atomic weights, it is found that K = 39, O = 16, and Cl = 35·5 hence the molecular weight of chlorate of potash is easily calculated.

One atomic weight of potassium, . .	39
,, ,, chlorine, . .	35·5
Three atomic weights of oxygen, . .	48
$KClO_3$ =	122·5

So that 122·5 grains of chlorate of potash would yield 48 grains of oxygen.

Since 16 grs. of oxygen measure 46·7 cubic inches (p. 21), the 48 grs. will measure 140 cubic inches.

Hence it is found that 122·5 grains of chlorate of potash would give 140 cub. in. of oxygen measured at 60° F. and 30 in Bar.

If one gallon (277·276 cub. in.) of oxygen be required, 242·6 grains of chlorate of potash must be used, or rather more than half an ounce.

Since the complete decomposition of the chlorate of potash alone requires a more intense heat than a glass vessel will usually endure, it is customary in preparing oxygen for chemical purposes to facilitate the

* Expressed in the form of an equation : $\underset{\text{Black oxide of manganese.}}{3MnO_2} = \underset{\text{Brown oxide of manganese.}}{Mn_3O_4} + O_2$.

† The oxygen contained in the chlorate of potash was derived from the lime employed in its manufacture (see Preparation of Chlorate of Potash). Its original source, therefore, was limestone.

decomposition of the chlorate by mixing it with about one-fifth of its weight of powdered black oxide of manganese, when the whole of the oxygen is given off at a comparatively low temperature, though the oxide of manganese itself suffers no change, and its action has not yet received any explanation which is quite satisfactory.

Fig. 32 shows a very convenient arrangement for preparing and collecting oxygen for the purpose of demonstrating its relations to combustion. A is a Florence flask,

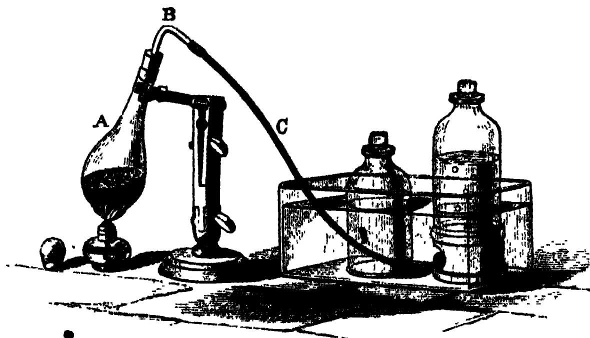


Fig. 32. - Preparation of oxygen.

in which the glass tube B is fixed by a perforated cork. C is a tube of vulcanised india-rubber. The gas-jar is filled with water, and supported upon a bee-hive shelf made of earthenware. If pint gas-jars be employed, 300 grains of the chlorate of potash, mixed with 60 grains of binoxide of manganese, will furnish a sufficient supply of gas for the ordinary experiments. The binoxide of manganese should be thoroughly dried by moderately heating it in a crucible before being mixed with the chlorate of potash. It is also advisable to test it by heating a little of it with the chlorate, since charcoal and sulphuret of antimony, which form very explosive mixtures with chlorate of potash, have sometimes been sold by mistake for binoxide of manganese. The heat must be moderated according to the rate at which the gas is evolved, and the tube C must be taken out of the water before the lamp is removed, or the contraction of the gas in cooling will suck the water back into the flask. The first jar of gas will contain the air with which the flask was filled at the commencement of the experiment. The oxygen obtained will have a slight smell of chlorine.

WATER.

30. *Synthesis of Water from its elements.*—It has been seen already (p. 20) that the combination of hydrogen with oxygen to form water is attended with great evolution of heat and consequent expansion, and hence the mixture of these gases is found to explode violently on contact with flame.

The experiment may be made safely in a soda-water bottle. The bottle is filled with water, and inverted with its mouth beneath the surface of the water; enough oxygen is then passed up into it to fill one-third of its volume; if the remainder of the water be then displaced by hydrogen, and the mouth of the bottle be presented to the flame of a spirit-lamp, a very violent explosion will result, attended with a vivid blue flash in the bottle. If the mouth of the bottle be presented towards a screen of paper, at a distance of 20 or 30 inches, the paper will be violently torn to pieces, bearing witness to the concussion between the expanded steam issuing from the bottle, and the external air.

If some of the mixture of oxygen, with twice its volume of hydrogen, be introduced into a capped jar (fig. 33), provided with a piece of caoutchouc tubing and a small glass tube, and pressed down in a trough of water, soap-bubbles may be inflated with

it, which will ascend rapidly in the air, and explode violently when touched with a flame, which must not, of course, be applied to the bubble until it is at some distance away from the tube, for fear of exploding the mixture in the jar.

31. In order to demonstrate the production of water in the explosion, the *Cavendish eudiometer** (fig. 34) is employed. This is a strong glass vessel, with a stopper

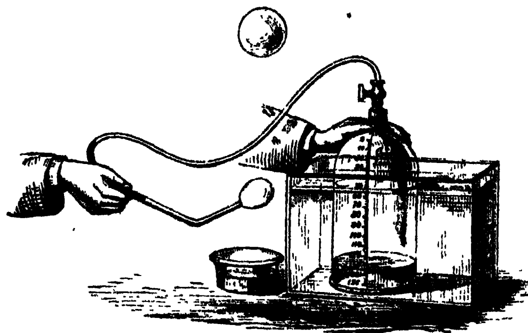


Fig. 33.

firmly secured by a clamp (A), and provided with two platinum wires (P), which pass through the stopper, and approach very near to each other within the eudiometer, so that the electric spark may easily be passed between them. By screwing the stopcock B into the plate of an air-pump, the eudiometer may be exhausted. It is then screwed on to the jar represented in fig. 35, which contains a mixture of two measures

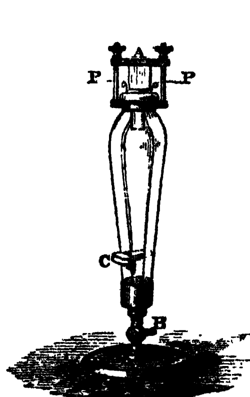


Fig. 34.

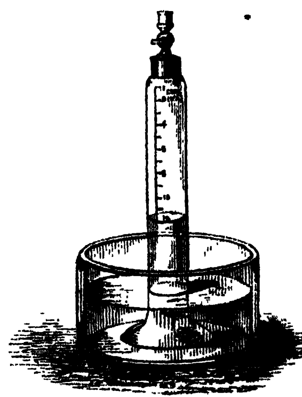


Fig. 35.

of hydrogen with one measure of oxygen, standing over water. On opening the stopcocks between the two vessels, the eudiometer becomes filled with the mixture, and the quantity which has entered is indicated by the rise of the water in the jar. The glass stop-clock C having been closed, to prevent the brass cap from being forced off by the explosion, the eudiometer is again screwed on to its foot, and an electric spark passed between the platinum wires, either from a Leyden jar or an induction coil, when the two gases will combine with a vivid flash of light,† attended with a very

* So named from εὔδιος, fine or clear, and μέτρον, a measure, because an instrument upon the same principle has been used to determine the degree of purity of the atmosphere. The eudiometer was employed by Cavendish about the year 1770, for the synthesis of water.

† Since the steam produced at the moment of combination is here prevented from expanding, the heat which would have expanded it is saved, so that the temperature is higher and the flash of light brighter than when the combination is effected in an open vessel.

slight concussion, since there is no collision with the external air. For an instant a mist is perceived within the eudiometer, which condenses into fine drops of dew, consisting of the water formed by the combination of the gases, which was here induced by the high temperature of the electric spark, as it was in the former experiment by the high temperature of the flame. If the gases have been mixed in the exact proportion of two measures of hydrogen to one measure of oxygen, the eudiometer will now be again vacuous, and if it be screwed on to the capped jar, may be filled a second time with the mixture, which may be exploded in the same manner.

The entire disappearance of the gases may be rendered obvious to the eye by exploding the mixture over mercury. For this purpose the mixed gases should be collected from water itself, which is strongly acidified with sulphuric acid, and decomposed in the *voltameter* (A, fig. 36) by the aid of five or six cells of Grove's battery. The voltameter contains two platinum plates (B), attached to the platinum

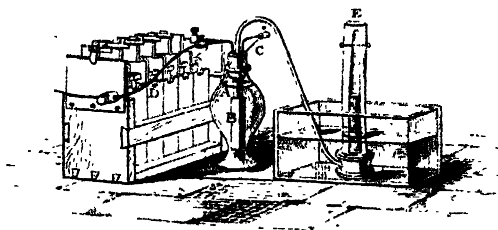


Fig. 36.—Detonating gas collected from voltameter.

wires C and D, which are connected with the opposite poles of the battery. The first few bubbles of the mixture of hydrogen and oxygen evolved having been allowed to escape, in order to displace the air, the gas may be collected in the small eudiometer (E), which has been previously filled with water. This eudiometer is a cylinder of very thick glass,* closed at one end, and having two stout platinum wires cemented into holes drilled near the closed end, the wires approaching sufficiently near to each other to allow the passage of the electric spark. Having been filled with the mixture of hydrogen and oxygen from the voltameter, the eudiometer is closed with the finger, and transferred to a basin containing mercury, where it is pressed firmly down upon a stout cushion of india-rubber, and the spark passed through the mixed gases, either from the coil or the Leyden jar. The combustion takes place with violent concussion, but without noise; and since the eudiometer is vacuous after the gases have combined, the cushion will be found to be very firmly pressed against its open end. On loosening the cushion, the mercury will be violently forced up into the eudiometer, which will be completely filled with it, proving that when an electric spark is passed through the mixture of two volumes of hydrogen and one volume of oxygen, no residue of gas remains.†

32. The knowledge of the volumes in which hydrogen and oxygen combine, is turned to account in the analysis of gases, to ascertain the proportion of hydrogen or oxygen contained in them. Suppose, for example, it be required to determine the amount of oxygen in a sample of atmospheric air; the latter is mixed with hydrogen, in more than sufficient quantity to combine with the largest proportion of oxygen which

* The bore of this eudiometer should be about half an inch in diameter, and the thickness of its sides about three-eighths of an inch; its length is 7 inches.

† This fact may also be demonstrated with the siphon eudiometer, shown in fig. 37, by confining about a cubic inch of the explosive mixture in the closed limb, over water, and stopping the open limb securely with a cork, so as to leave a space filled with air between the cork and the water. The eudiometer must be very firmly fixed on a stand, or it will be broken by the concussion. After it has been proved, it may be held in the hand, as in the figure. By firing mixtures of hydrogen and oxygen, in different proportions, in the same manner, it may be shown that any excess of either gas above the ratio of 2H : 1O will remain uncombined after the explosion. Care is required in these experiments, since eudiometers are often burst by the explosion of the mixture of 2 vols. of hydrogen with 1 vol. of oxygen.

could be present, and when the combination has been induced by the electric spark, the volume of gas which has disappeared (2 vols. H + 1 vol. O) has only to be divided by three to give the volume of the oxygen.

A bent eudiometer (fig. 37) is generally employed for this purpose. Having been completely filled with water, it is inverted in the trough, and the specimen of air is introduced (say 0·5 cubic inch). The open limb is then closed by the thumb, and the eudiometer turned so as to transfer the air to the closed limb. A stout glass rod is thrust down the open limb, so as to displace enough water to equalise the level in both limbs, in order that the volume of the air may not be diminished by the pressure of a higher column of water in the open limb. The volume of the included air having been accurately noted, the open limb of the tube is again filled up with water, inverted in the trough, and a quantity of hydrogen introduced, equal to about half the volume of the air. This having been transferred, as before, to the closed limb, the columns of water are again equalised, and the volume of the mixture of air and hydrogen ascertained. The open limb is now firmly closed with the thumb, and the electric spark passed through the mixture, either from the Leyden jar or the induction coil. On removing the thumb, after the explosion, the volume of gas in the closed limb will be found to have diminished very considerably. Enough water is poured into the open limb to equalise the level, and the volume of gas is observed. If this volume be subtracted from the volume before explosion, the volume of gas which has disappeared will be ascertained, and one-third of this will represent the oxygen, which has condensed with twice its volume of hydrogen into the form of water. Thus the numbers recorded will be—

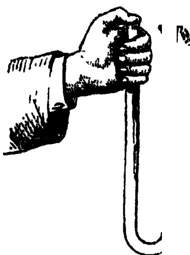


Fig. 37.
Siphon eudiometer.

Volume of air analysed, ...	0·50 cub. in.
Volume of air mixed with hydrogen, ...	0·75 ,,
After explosion, ...	0·45 ,,
Difference, ($\frac{2}{3}$ H and $\frac{1}{3}$ O)	·30 ,,

·30, divided by 3 = ·10 cub. in. of oxygen.

It is evident that the volume of hydrogen contained in a gas might be ascertained in a similar manner, by exploding with oxygen, and taking two-thirds of the gas which had disappeared in the form of water to represent the volume of hydrogen.

In exact experiments, a correction would be required for any variation of the temperature or barometric pressure during the progress of the analysis.

33. It will have been observed, in the experiment upon the synthesis of water in the Cavendish eudiometer, that the volume of water obtained is very small in comparison with that of the gases before combination, nearly 2600 volumes of the mixed gases being required to form one volume of the liquid. But it is evident that no comparison can, with propriety, be made between the volume of a compound, in the liquid or solid state, and that of its components in the gaseous state, since the particles of the former are under the influence of the cohesive force from which those of the latter are free. For the purposes of such a comparison the volume of the compound body must be taken under precisely the same physical conditions as the volume of its components.

If the mixture of hydrogen and oxygen be measured and exploded at a temperature above the boiling point of water, it is found that the steam produced occupies two-thirds of the volume of the mixed gases, measured at the same temperature and atmospheric pressure. Hence, *two volumes*

of hydrogen combine with one volume of oxygen to form two volumes of aqueous vapour, at the same temperature and pressure.

The combination of hydrogen and oxygen in a vessel heated above the boiling-point of water is effected in the apparatus contrived by Dr Hofmann, and represented in fig. 38, where the closed limb of the eudiometer is surrounded by a tube through which the vapour of boiling *fousel oil*, having a temperature of 270° F., is passed from a flask connected with the wide tube by a cork and a short wide piece of bent glass tubing, jacketed with caoutchouc to prevent loss of heat. The vapour of fousel oil passes out of the wide tube through the tube *t* which enters the cork at the bottom, and conducts the vapour into a glass worm (*w*) immersed in a jar through which cold water is allowed to flow, as shown by the arrows. The closed limb of the eudiometer having been filled with mercury, a small quantity of the mixture of hydrogen and oxygen obtained from the voltameter (fig. 36) is introduced into it through a tube passed down the open limb, the displaced mercury being run out through the tube *c*, which is closed by a nipper-tap. The closed limb is then heated by the vapour, and the mercury in the two limbs levelled from time to time by running a little out through *c*, until the gas in the closed limb no longer expands. Its volume is then observed, an inch more mercury poured into the open limb, which is then tightly closed by a cork, and the spark from the induction-coil is passed by the wires − and + . After the explosion the cork is removed, and the mercury levelled in the two limbs, when the volume of the steam will be found to be just two-thirds of the volume of the gas before explosion. On cooling down, the steam condenses, and the mercury entirely fills the closed limb of the eudiometer.

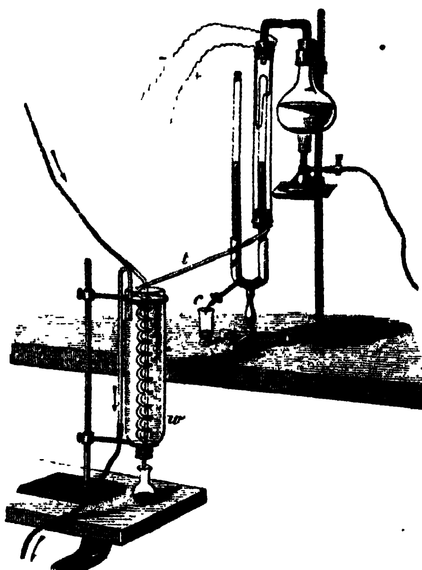


Fig. 38.—Synthesis of water above 212°.

That 2 volumes of steam should contain 2 volumes of hydrogen and 1 volume of oxygen would appear, on physical grounds, impossible, since two bodies cannot occupy the same space at the same time; but it must be remembered that the two bodies in question have lost their individuality in consequence of their chemical combination, by which they have become one body—water.

A distinction must be carefully drawn between the *ultimate physical particles* (*molecules*) and the *ultimate chemical particles* (*atoms*) of any form of matter. The smallest conceivable particle of steam, incapable of further mechanical subdivision, would yet be capable of being divided by chemical means into 2 atoms of hydrogen and 1 atom of oxygen.

On comparing steam with hydrogen, it is found that they are expanded in the same degree by heat, and contracted in the same degree by cold.

or pressure, provided that the steam is always at a temperature remote from its condensing point. Hence it appears that *equal volumes of steam and hydrogen contain the same number of molecules or ultimate physical atoms.*

(1.) Suppose V volumes of steam to contain M molecules,
(2.) Then V volumes of hydrogen contain M molecules;
(3.) But M molecules of steam contain 2 M atoms of hydrogen;
(4.) Therefore (by 1), V volumes of steam contain 2 M atoms of hydrogen.
(5.) But V volumes of steam contain V volumes of hydrogen;
(6.) Therefore, V volumes of hydrogen contain 2 M atoms of hydrogen,
(7.) And (by 2) V volumes of hydrogen contain M molecules;
(8.) Therefore, 2 M atoms of hydrogen = M molecules,
or 2 atoms of hydrogen = 1 molecule.

By precisely similar reasoning it may be shown that the molecule, or smallest conceivable physical particle of oxygen, must be composed of 2 atoms of oxygen. Hence, the important conclusion is arrived at that *the molecule or ultimate physical particle of matter, whether elementary or compound, occupies, in the state of gas or vapour, twice the volume occupied by an atom of hydrogen.* Thus,

			Volume.	Weight.
Atom of hydrogen	=	H	1	1
Atom of oxygen		O	1	16
Molecule of hydrogen		H_2	2	2
Molecule of oxygen		O_2	2	32
Molecule of steam		H_2O	2	18

Since the molecule of a compound body in the state of gas or vapour occupies 2 volumes, and the specific gravity is the weight of 1 volume, *half the molecular weight of a compound gas or vapour will give its specific gravity referred to hydrogen as the standard.*

Thus, the molecular weight of steam being 18, its specific gravity (H = 1) would be 9.

If the specific gravity in relation to air be required, it may be obtained by multiplying the specific gravity referred to hydrogen by 0·0692, which represents the specific gravity of hydrogen referred to air as the unit.

The above considerations help to explain the indisposition of hydrogen and oxygen to combine at the ordinary temperature, for the molecule of hydrogen (H_2) combines with the atom of oxygen, so that the two atoms of this element which are contained in the molecules must be separated in order to combine with the hydrogen.

34. The synthesis of water by weight cannot be effected with accuracy by weighing the gases themselves, on account of their large volume. It is, therefore, accomplished by passing an indefinite quantity of hydrogen over a known weight of pure hot oxide of copper, when the hydrogen combines with the oxygen of the oxide to form water. The loss of weight suffered by the oxide of copper gives the amount of oxygen; and if this be deducted from the weight of the water, that of the hydrogen will be ascertained.

The apparatus employed for this purpose is represented in fig. 39. *h* is the bottle,

in which hydrogen is generated from diluted sulphuric acid and zinc; the gas passes in *p* through solution of potash, which absorbs any sulphuretted hydrogen; then through *s*, containing pumice stone (used on account of its porous character), saturated with a strong solution of nitrate of silver, which removes arsenic and antimony from the hydrogen; the gas then passes through *vv*, containing pumice saturated with oil

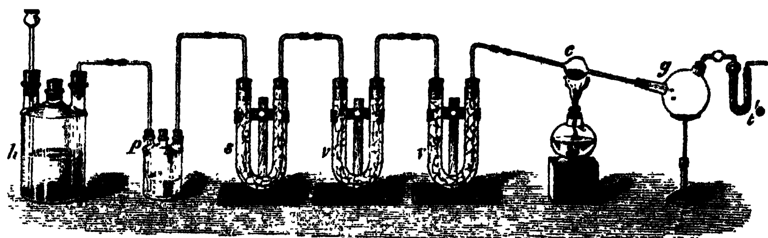


Fig. 39.—Synthesis of water by weight.

of vitriol to absorb moisture. The bulb *c*, with the oxide of copper, is weighed before and after the experiment, as are the globe *g*, for condensing the water, and the tube *t*, containing pumice and oil of vitriol, to absorb the aqueous vapour. Of course, the bulb *c* must not be heated until the hydrogen has displaced all the air from the apparatus.

35. It is evident that, although hydrogen is generally designated the combustible gas, and oxygen the supporter of combustion, the application of these terms depends entirely upon circumstances, since the phenomenon of combustion is a reciprocal operation in which both elements have an equal share.

This may be illustrated by a simple experiment. The hydrogen and oxygen reservoirs,* H and O, fig. 40, are connected with two bent glass tubes passing through a cork into an ordinary lamp glass *c*, upon the upper opening of which a piece of tin-plate is laid. In order to prevent the ends of the glass tubes from being fused by the burning gases, little platinum tubes, made by rolling up pieces of platinum foil, are placed in the orifices, and the glass is melted round them by the blowpipe flame. The hydrogen being lighted, and the oxygen turned on to about the same extent, the lamp-glass is placed over the cork, when the hydrogen burns steadily. If the oxygen be slowly turned off, the flame will gradually leave the hydrogen tube and come over to the oxygen, which will continue burning in the atmosphere of hydrogen. By again turning on the oxygen, the flame may be sent over to the hydrogen tube. With a little care the flame may be made to occupy an intermediate position between the two burners, and to leap from one to the other at pleasure.

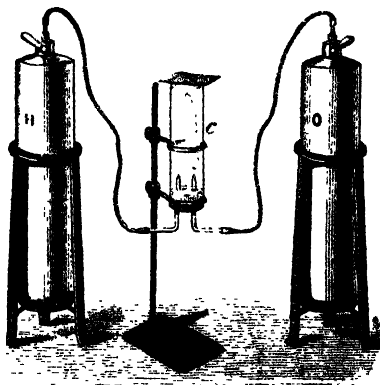


Fig. 40. – Reciprocal combustion.

36. The great energy with which hydrogen combines with oxygen is turned to account for the purpose of producing the highest temperature which can be obtained by any chemical process.

The *oxyhydrogen* blowpipe (fig. 41) is an apparatus for burning a jet of hydrogen mixed with half its volume of oxygen. The gases are supplied from separate gas-

* These are the wrought iron vessels in which hydrogen and oxygen are condensed under the pressure of a few atmospheres by Mr Orchard of Kensington. They are far more convenient than gas-bags or gas-holders.

holders (or bags with pressure-boards and weights) through the tubes H and O, which conduct them into the brass sphere B. Each of these tubes is provided with a valve of oiled silk opening outwards, so as to prevent the passage of either gas into the receptacle containing the other. The tube A is stuffed with thin copper wires, which would rapidly conduct away the heat and extinguish the flame of the mixed gases burning at the jet, should it tend to pass back and ignite the mixture in B. The stop-cocks D and E allow the flow of the gases to be regulated so that they may mix in the right proportions. If the hydrogen be kindled first, it will be found that, as soon as the oxygen is turned on, the flame is reduced to a very much smaller volume, because the undiluted oxygen required to maintain it occupies only one-fifth of the volume of the atmospheric air from which the hydrogen was at first supplied with oxygen. The heat developed by the combustion being therefore distributed over a much smaller area, the temperature at any given point of the flame must be much higher, and very few substances are capable of enduring it without fusion.* Lime is one of these; and if a cylinder of lime be supported, as at L, fig. 41, in the focus of the flame, its particles become heated to incandescence, and a light is obtained which is visible at night from very great distances, so as to be well adapted for signalling and lighthouses. For such purposes coal-gas is often used instead of hydrogen (*oxycalcium* light).

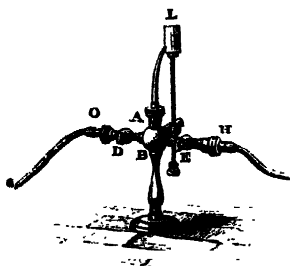
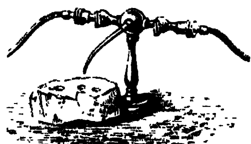


Fig. 41.—Oxyhydrogen blowpipe.

If a shallow cavity be scooped in a lump of quicklime, a few scraps of platinum placed in it, and exposed to the oxyhydrogen flame (fig. 42), a fused globule of platinum of very considerable size may be obtained in a few seconds. By employing a little furnace made of lime, Deville has succeeded in fusing platinum in quantities sufficient to cast large ingots, a result unattainable by any other furnace. Pipeclay, which resists the action of all ordinary furnace-heats, may be fused into a glass in this flame, whilst gold and silver are instantaneously melted, and vaporised into a dense smoke.


Fig. 42.

37. In its chemical relations to other elements, hydrogen is diametrically opposed to oxygen. Whereas the latter combines directly with the greater number of the elements, hydrogen will enter into direct combination with very few; *oxygen, chlorine, bromine, iodine, carbon*, and *sulphur* (the three last with difficulty), are the only elements which unite in a direct manner with hydrogen, and of these only chlorine and bromine combine with hydrogen at the ordinary temperature, though not without exposure to light. Again, whilst fluorine is not known to form any compound with oxygen, its combination with hydrogen (hydrofluoric acid) is one of the most stable compounds known, and it may be safely asserted that fluorine in the free state would combine with hydrogen even more readily than chlorine does. All the metals form compounds with oxygen, but very few combinations of metals with hydrogen have been obtained. Indeed, in its relations to other elements, hydrogen closely resembles the metals, though it does not fall within the definition of a metal given above, since it does not form a base with oxygen, and its combinations with the salt-radicals (chlorine, &c.) are acids, and not salts.

In the course of some experiments upon the power possessed by metals of absorbing (or *occluding*) gases at high temperatures and retaining them after cooling, Graham found that the metal palladium could be made to absorb nearly one thousand times its volume of hydrogen at the temperature of boiling water. Finding that the metallic characters of the palla-

* The temperature of this flame has been estimated at about 14,000° F.

dium were not destroyed, as would be the case if it had combined with a non-metallic substance, Graham was inclined to believe in the metallic character of hydrogen, or *hydrogenium*, as he termed it. But since the hydrogen is very easily recovered by moderately heating the palladium, and the absorption of large volumes of gases by solid bodies without alteration in the properties of the latter, is not at all uncommon, the conclusion is scarcely justified. The hydrogen associated with palladium, however, has far more active properties than ordinary hydrogen, for it often combines spontaneously with the oxygen of the air, and will unite with chlorine and iodine even in the dark.

38. Chemical Relations of Water to other Substances.—In its chemical relations water presents this very remarkable feature, that, although it is an *indifferent oxide*, its combining tendencies extend over a wider range than those of any other compound. Its combinations with other substances are generally called *hydrates*. Water combines with two of the elementary substances, viz., chlorine and bromine, forming an exception to the general rule, that *combination does not take place between elementary and compound bodies*. No other element is even *dissolved* by water in any considerable quantity. One part of iodine is dissolved by 500 parts of cold water, but no chemical combination appears to take place. Oxygen, hydrogen, and nitrogen are dissolved by water in very small quantity, but become only mechanically diffused through it, and do not enter into chemical combination.

When water acts upon a compound body, it may either effect a *simple solution*, or may enter into chemical combination with it.

Simple solution appears to be a purely physical phenomenon, not accompanied, of necessity, by any chemical action. The dissolved substance, in such cases, is otherwise unchanged in properties, and there is no manifestation of heat, as in cases of chemical combination. On the contrary, there is a reduction of temperature, such as is always noticed in the merely physical change from the solid to the liquid form. For example, common saltpetre (nitre or nitrate of potash), when shaken with water, is rapidly dissolved, the water becoming sensibly colder. If fresh portions of saltpetre be added till the water is unable to dissolve any more, it will be found that 1000 grs. of water (at 60° F.) have dissolved about 300 grs. of saltpetre. Such a solution would be called a *cold saturated solution* of saltpetre. If the solution be set aside in an open vessel, the water will slowly pass off in vapour, and the saltpetre will be gradually deposited, its particles arranging themselves in the regular geometrical shape of the six-sided prism, which is its common *crystalline form*. The crystals of saltpetre do not contain any water; they are *anhydrous*.



Fig. 43.

If saltpetre be added to boiling water (in a porcelain evaporating dish, fig. 43), and stirred (with a glass rod) until the water refuses to dissolve any more, 1000 grs.* of water will be found to have dissolved about 2000 grs.; this would be called a *hot saturated solution*.

As a general rule, solids are dissolved more quickly and in larger quantity by hot water than by cold.

One of the commonest methods of *crystallising* a solid substance consists in dissolving it in hot water, and allowing the solution to cool slowly. The more slowly it cools, the larger and more symmetrical are the crystals. A hot saturated solution is not generally the best for crystallising, because it deposits the dissolved body too rapidly. Thus, the hot solution of saltpetre prepared as above would solidify to a mass of minute crystals on cooling; but if 1000 grs. of saltpetre be dissolved in 4 measured ounces of boiling water, it will form crystals of two or three inches long when slowly cooled (in a covered vessel). If the solution be stirred while cooling, the crystals will be very minute, having the appearance of a white powder.

Some solids, however, refuse to crystallise, even from a hot saturated solution, if it be kept absolutely undisturbed.

Sulphate of soda affords a good example of this. If the crystallised sulphate be added to boiling water in a flask, as long as it is dissolved, the water will take into solution more than twice its weight of the salt, yielding a solution which boils at 220° F. If this solution be allowed to cool in the open flask, an abundant crystallisation will take place, for cold water will dissolve only about one-third of its weight of crystallised sulphate. But if the flask (which should be globular) be tightly corked whilst the solution is boiling, it may be kept for several days without crystallising, although moved about from one place to another. In this condition the solution is said to be *super-saturated*. On withdrawing the cork, the air entering the partly vacuous space above the liquid will be seen to disturb the surface slightly, and from that point beautiful prismatic crystals will shoot through the liquid until the whole has become a nearly solid mass. A considerable elevation of temperature is observed, consequent upon the passage from the liquid to the solid form. If the solution of sulphate of soda be somewhat weaker, containing exactly two-thirds of its weight of the crystals, it may be cooled without crystallising, even in vessels covered with glass plates, but a touch with a glass rod will start the crystallisation immediately.*

Minute solid particles (*nuclei*) derived from the air appear to be instrumental in causing the crystallisation of super-saturated solutions. If the solution of sulphate of soda containing two-thirds of its weight of the crystallised salt be allowed to cool in a flask closed by a cork furnished with two tubes closed with plugs of cotton wool, it will be found that on withdrawing the plugs and blowing air through one of the tubes dipping into the solution, crystallisation does not take place, apparently because the air has been deprived of the particles capable of causing it; for if air be blown through the same solution with the bellows, it solidifies almost instantaneously.

A most beautiful illustration of the power of unfiltered air to start crystallisation is afforded by a solution of alum which has been saturated at 194° F., and allowed to cool in a flask, the mouth of which is closed by a plug of cotton wool. In this state it may be kept for weeks without crystallising, but on withdrawing the plug, crystallisation will be seen to commence at a few points on the surface immediately under the opening of the neck, and will spread slowly from these, octahedral crystals of alum of half an inch or more in diameter being built up in a few seconds, the temperature, at the same time, rising very considerably.

In the laboratory, stirring is always resorted to in order to induce crystallisation, if it does not take place spontaneously. Thus it is usual to test for potash in a solution by adding tartaric acid, which should cause the formation of minute crystals of *bitartrate of potash* (*cream of tartar*), but the test seldom succeeds unless the solutions are briskly stirred together with a glass rod. An amusing illustration of this is afforded by pouring a solution of tartaric acid into a solution of saltpetre, and allowing the clear mixture to run over a large plate of glass. Letters traced on the glass with the finger will now be rendered visible by the deposition of the crystals of bitartrate of potash upon the glass.

39. The crystals of sulphate of soda produced in the above experiments contain, in a state of combination with the salt, more than half their weight of water. Their composition is—

* It is very remarkable that, if the glass rod has been recently heated, it will not cause the crystallisation even after it has been cool for some time.

Anhydrous sulphate of soda ($Na_2O.SO_3$)	142 parts,	or one molecule,
Water	180 ,,	or ten molecules,

as expressed by the formula $Na_2O.SO_3.10H_2O$. If some of the crystals be pressed between blotting paper to remove adhering water, and left exposed to the air, they will gradually *effloresce*, or become covered with a white opaque powder. This powder is the anhydrous sulphate of soda into which the entire crystals would ultimately become converted by exposure to air. Since most crystals containing water have their crystalline form destroyed or modified by the loss of the water, it is commonly spoken of as *water of crystallisation.*

Coloured salts, containing water of crystallisation, generally change colour when the water is removed. The *sulphate of copper* (*blue stone*) affords an excellent example of this. The beautiful blue prismatic crystals of this salt contain

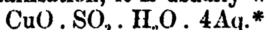
Anhydrous sulphate of copper ($CuO.SO_3$)	159·5 parts,	or one molecule,
Water	90·0 ,,	or five molecules.

as expressed by the formula $CuO.SO_3.5H_2O$.

When these are exposed to the air at the ordinary temperature they remain unchanged; but if heated to the boiling-point of water, they become opaque, and may be easily crumbled down to a white powder. This powder contains

Anhydrous sulphate of copper ($CuO.SO_3$)	159·5 parts,	or one molecule,
Water	18 ,,	or one molecule,

and would therefore be represented by $CuO.SO_3.H_2O$. The four molecules of water, which have been expelled, constituted the water of crystallisation, upon which the form and colour of the sulphate of copper depend. If the white powder be moistened with water, combination takes place, with great evolution of heat, and the blue colour is reproduced. The one molecule of water which still remains, is not expelled until the salt is heated to 390° F. (199° C.), proving that it is held to the sulphate of copper by a more powerful chemical attraction. On this account it is spoken of as *water of constitution*, and in order that the formula of the salt may exhibit the difference between the water of constitution and of crystallisation, it is usually written



$$CuO\,.\,SO_3\,.\,H_2O\,.\,4Aq.*$$

(DEFINITION.—*Water of crystallisation* of salts is that which is generally expelled at 212° F. (100° C.), and is connected with the form and colour of the crystals. *Water of constitution* is not generally expelled at 212° F., and is in more intimate connection with the chemical properties of the salt.)

Several of the so-called *sympathetic inks* employed for writings which are invisible until heated, depend upon the change of colour which results from the loss of water of crystallisation. Characters written with a weak solution of chloride of cobalt and allowed to dry, are very nearly invisible, since the pink colour of so small a quantity of the salt is scarcely noticed; but on warming the paper, the pink hydrated chloride of cobalt ($CoCl_2.2Aq.$) loses its water of crystallisation, and the blue anhydrous chloride of cobalt is produced. On exposure to air this again absorbs water, and the writing fades away.

Some salts have so great a tendency to combine with water, that they

* *Aqua*, water.

become moist or *deliquesce* when exposed to air. This *deliquescence* is exhibited in a marked degree by *chloride of calcium*, and its great attraction for water is turned to advantage in drying air and other gases by passing them through tubes filled with the salt.

40. Most bases are capable of combining with water to form hydrates, as exemplified in the slaking of lime. Anhydrous lime or quick-lime (CaO), when wetted with water, combines with it, evolving much heat, and crumbling to a loose bulky powder, which is hydrate of lime or slaked lime ($CaO.H_2O$). At a red heat the water is expelled, and anhydrous lime remains.

The hydrates of potash, soda, and baryta, however, do not lose their water when heated, which has led some chemists to entertain the belief that they do not really contain water as such, but that they have been formed from water by the substitution of a metal for a portion of its hydrogen. Upon this view, the hydrate of potash, instead of being represented by the formula $K_2O.H_2O$, would be KHO, or water (H_2O), in which potassium has been substituted for half the hydrogen.

41. Nearly all the acids are capable of forming hydrates. Indeed, as a general rule, the hydrated form of an acid is that in which it is commonly obtained and used, the anhydrous acid being usually of very secondary importance. Thus, the liquid used under the name of concentrated sulphuric acid is the hydrate of that acid ($H_2O.SO_3$), the anhydrous sulphuric acid (SO_3) being a crystalline solid of no use except to the chemist, and not manifesting any acid properties until brought into contact with water, with which it combines with evolution of much heat. The hydrated sulphuric acid ($H_2O.SO_3$) does not lose its water when heated, but distils unchanged, and some chemists are of opinion that the hydrogen is not contained in it in the form of water, but that the so-called hydrated sulphuric acid should be represented as H_2SO_4, so as not to indicate that it contains water. The acid is thus represented as a *unitary* compound (formed of one group), instead of a *binary* compound of the groups H_2O and SO_3. Convenient as this view is sometimes found in notation and in theoretical speculations, the circumstance that SO_3 is known in the separate state, and yields the hydrated sulphuric acid when brought in contact with water, causes the latter view still to find favour among many practical chemists.

The hydrated sulphuric acid ($H_2O.SO_3$) has a very powerful attraction for more water, which leads to its employment in the laboratory for drying air and gases, as well as for producing many chemical changes which depend upon the abstraction of water or its elements (*dehydration*). If concentrated sulphuric acid (*oil of vitriol*) be poured into water, the mixture will become very hot, in consequence of the combination between the two liquids. The water should be stirred whilst the acid is being poured in, as the sudden mixture of considerable quantities might cause danger from the projection of the liquid.

42. Water from Natural Sources.—Pure water is not found in nature. Rain is the purest form of natural water, but contains certain gases which it collects from the atmosphere during its fall. As soon as it reaches the earth, it begins to dissolve small portions of the various solid materials with which it comes in contact, and thus becomes charged with salts and other substances to an extent varying, of course, with the

nature of the soils and rocks which it has touched, and attaining its highest point in sea water, which contains a larger proportion of saline matters than water from any other natural source. Ice, when melted, affords nearly pure water, since, when water containing salts is partially frozen, these are left dissolved in the uncongealed water.

If a quantity of rain, spring, river, or sea water be boiled in a flask furnished with a tube also filled with the water, and passing under a gas cylinder standing in a trough of the same water (fig. 44), it will be found to give off a quantity of gas which was previously held in solution by the water, and is now set free because *gases are less soluble in hot than in cold water.* The quantity of this gas will vary according to the source of the water, but it will always be found to contain the gases existing in atmospheric air, viz., nitrogen, oxygen, and carbonic acid. One gallon of rain water will generally furnish about 4 cubic inches of nitrogen, 2 cubic inches of oxygen, and 1 cubic inch of carbonic acid. It is worthy of remark, that the nitrogen and oxygen have been dissolved by the water, not in the proportions in which they exist in the atmosphere (4 N : 1 O), but in the proportions in which they ought to be dissolved, if it be true that they exist in the air in the condition of mere mechanical admixture. The oxygen thus carried down from the air by rain appears to be serviceable in maintaining the respiration of aquatic animals, and in conferring upon river waters a self-purifying power, by acting upon certain organic matters which would probably prove hurtful to animals, and converting them into harmless products of oxidation. In the cases of rivers contaminated with the sewage of towns, this action of the dissolved oxygen is probably of great importance. The carbonic acid dissolved in rain water also probably serves some useful purposes in the chemical economy of Nature. (See *Carbonic Acid.*)

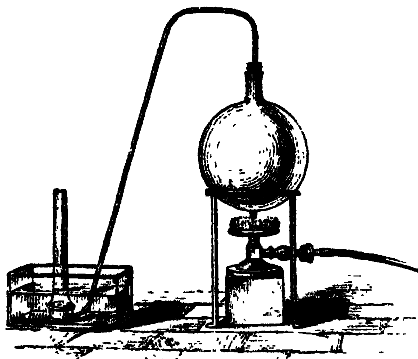


Fig. 44.

43. The waters of wells, springs, and rivers, and especially those of the two first-named sources, differ very much from each other, according to the nature of the layers of rock or earth over or through which they have passed, and from which they dissolve a great variety of substances, some of which are familiar to us in daily life, while others are only met with in chemical collections. Under the former head may be enumerated Glauber's salt (sulphate of soda), common salt (chloride of sodium), Epsom salt (sulphate of magnesia), gypsum (sulphate of lime), chalk (carbonate of lime), common magnesia (carbonate of magnesia), carbonic acid, and silica.

Among the substances known only to the chemist, may be mentioned sulphuretted hydrogen, sulphate of potash, chloride of potassium, chloride of calcium, chloride of magnesium, phosphate of lime, bromides and

iodides of calcium and magnesium (rarely), alumina (probably sulphate of alumina), carbonate of iron, and certain vegetable substances.*

The well waters of certain localities (as, for example, those of large towns) also frequently contain salts of nitric and nitrous acids, and of ammonia.

The waters of springs and rivers do not differ very materially from well waters as to the nature of the substances which they contain, though, in the case of river waters more particularly, the quantity of these substances is materially influenced by the conditions of rapid motion and exposure to air under which such waters are placed.

Household experience has established a classification of the waters from natural sources into *soft* and *hard* waters—a division which depends chiefly upon the manner in which they act upon soap. If a piece of soap be gently rubbed in soft water (rain water, for example) it speedily furnishes a froth or *lather*, and its cleansing powers can be readily brought into action; but if a hard water (spring water) be substituted for rain water, the soap must be rubbed for a much longer time before a lather can be produced, or its effect in cleansing rendered evident; a number of white curdy flakes also make their appearance in the hard water, which were not seen when soft water was used. The explanation of this difference is a purely chemical one.

Soap is formed by the combination of a fatty acid with an alkali; it is manufactured by boiling oil or fat with potash or soda, the former for soft, the latter for hard soaps. In the preparation of ordinary hard soap, the soda takes from the oil or fat two acids,—*stearic* and *oleic* acids,—which exist in abundance in most varieties of fat, and unites with them to form soap, which in chemical language would be spoken of as a mixture of *stearate* and *oleate of soda*.

If soap be rubbed in soft water until a little of it has dissolved, and some Epsom salts (sulphate of magnesia) be dissolved in water, and poured into the soap water, curdy flakes will be produced, as when soap is rubbed in hard water, and the soap water will lose its property of frothing when stirred; the sulphate of magnesia has decomposed the soap, the soda contained in the latter has combined with the sulphuric acid existing in the sulphate of magnesia, to form a sulphate of soda which remains dissolved in the water, while the magnesia, uniting with the stearic and oleic acids, produces the insoluble curdy flakes, which consist of stearate and oleate of magnesia.

Similar to the effect of the sulphate of magnesia is that of hard waters; their hardness is attributable to the presence of the different salts of lime and magnesia, all of which decompose the soap in the manner exemplified above; the peculiar properties of the soap in forming a lather and dissolving grease can, therefore, be manifested only when a sufficient quantity has been employed to decompose the whole of the salts of lime and magnesia contained in the quantity of water operated on, and thus a considerable amount of soap must be rendered useless when hard water is employed.

On examining the interior of a kettle in which spring, well, or river water has been boiled, it will be found to be coated more or less thickly with a *fur* or incrustation, generally of a brown colour, and the harder

* Although it is certainly known that the acids and bases capable of forming the salts here enumerated may be detected in spring and river waters, their exact distribution amongst each other is still a matter of uncertainty.

the water, the more speedily will this incrustation be deposited. A chemical examination shows this deposit to consist chiefly of carbonate of lime, in the form of minute crystals, which may be discovered by the microscope; it usually contains, in addition, some carbonate of magnesia, sulphate of lime, and small quantities of sesquioxide of iron (rust), and vegetable matter, the last two substances imparting its brown colour. In order to explain the formation of this deposit, it is necessary to become acquainted with the particular condition in which the carbonate of lime exists in natural waters. Carbonate of lime is hardly dissolved to any perceptible extent by pure water, though it may be dissolved in considerable quantity by carbonic acid. This statement, which is of great importance in connection with natural waters, may be verified in the following manner. A little slaked lime is well shaken up in a bottle of distilled or rain water, which is afterwards set aside for an hour or two; as soon as that portion of the lime which has not been dissolved has subsided, the clear portion is carefully poured into a glass, and a little soda-water or solution of carbonic acid in water is added to it; the first addition of the carbonic acid to the lime water causes a milkiness, due to the formation of minute particles of carbonate of lime, by the union of the carbonic acid with the lime; this carbonate of lime, being insoluble in the water, separates from it, or *precipitates* and impairs the transparency of the liquid; a further addition of carbonic acid water renders the liquid again transparent, for the carbonic acid dissolves the carbonate of lime which has separated, forming, in the opinion of some chemists, a definite chemical compound, the *bicarbonate of lime*, which contains twice as much carbonic acid as the carbonate; since, however, this bicarbonate of lime has not been separated from the water in a pure state, it is safer to regard it merely as a solution of carbonate of lime in free carbonic acid.

If this clear solution be introduced into a flask, and boiled over the spirit-lamp or gas-flame, it will again become turbid, for the free carbonic acid will be expelled by the heat, and the carbonate of lime will be deposited, not now, however, in so fine a powder as before, but in small hard grains which have a tendency to fix themselves firmly upon the sides of the flask, and, when examined by the microscope, are seen to consist of small crystals.

In a similar manner, when natural waters are boiled, the free carbonic acid which they contain is expelled in the gaseous state, and the carbonates of lime, magnesia, and oxide of iron are precipitated, since they are insoluble in water which does not contain carbonic acid. But, by the ebullition of the water, a portion of it has been dissipated in vapour, and if there be much sulphate of lime present, the quantity of water left may not be sufficient to retain the whole of that salt in solution; and this is the more likely to happen, because sulphate of lime requires about 400 parts of water to dissolve it;* a quantity of sulphate of lime, then, is liable to be deposited together with the carbonates of lime, magnesia, and oxide of iron, and, should the water contain much vegetable matter, this is also often deposited in an insoluble condition, the whole eventually forming together a hard compact mass, composed of successive thin layers, on the bottom and sides of the vessel in which the water has been boiled.

* Sulphate of lime has been found nearly insoluble in water having a higher temperature than 212° F., as would be the case in boilers worked under pressure, so that it would readily be deposited. It is said that waters containing little or no sulphate of lime yield a loose and friable deposit.

The "furring" of a kettle is objectionable, chiefly in consequence of its retarding the ebullition of the water, since the deposit is a very bad conductor of heat, and therefore impedes the transmission of heat from the fire to the water; hence the common practice of introducing a round stone or marble into the kettle, in order, by its perpetual rolling, to prevent the particles of carbonate of lime from forming a compact layer. In steam boilers, however, even more serious inconvenience than loss of time sometimes arises if this deposit be allowed to accumulate, and to form a thick layer of badly conducting material on the bottom of the boiler, since the latter is then liable to become red hot, and should the incrustation happen to crack, and allow the water to reach the red hot metal, so violent a disengagement of steam follows, that boilers have been known to burst under the sudden pressure. But even though this calamity be escaped, the wear and tear of the boiler is very much increased in consequence of the formation of this deposit, since its hardness often renders it necessary to détach it with the hammer, much to the injury of the iron boiler-plates, which are also subject to increased oxidation and corrosion, in consequence of the high temperature which the incrustation permits them to attain by preventing their contact with the water. Many propositions have been brought forward for the prevention of these incrustations; some substances have been used of which the action appears to be purely mechanical, in preventing the aggregation of the deposited particles. Clay, saw-dust, and other matters have been employed with this view; but the action of sal-ammoniac, which has also been found efficacious, must be explained upon purely chemical principles. When this salt is boiled with carbonate of lime, mutual decomposition ensues, resulting in the production of chloride of calcium and carbonate of ammonia, of which salts the former is very soluble in water, while the latter passes off in vapour with the steam.*

The deposit formed in boilers fed with sea water consists chiefly of sulphate of lime and hydrate of magnesia, the latter resulting from the decomposition of the chloride of magnesium present in sea water.

The incrustations formed in cisterns and pipes by hard water are also produced by the carbonates of lime and magnesia deposited in consequence of the escape of the free carbonic acid which held them in solution. Many interesting natural phenomena may be explained upon the same principle. The so-called *petrifying springs*, in many cases, owe their remarkable properties to the considerable quantity of carbonate of lime dissolved in carbonic acid which they contain; when any object, a basket, for example, is repeatedly exposed to the action of these waters, it becomes coated with a compact layer of carbonate of lime, and thus appears to have suffered conversion into limestone. The celebrated waters of the Sprudel at Carlsbad, of San-Filippo in Tuscany, and of Saint Allyre in Auvergne, are the best instances of this kind.

The *stalactites* and *stalagmites*,† which are formed in certain caverns or natural grottoes (fig. 45), afford beautiful examples of the gradual separation of the carbonate of lime from water charged with carbonic acid. Each drop of water, as it trickles through the roof of the cavern, becomes surrounded with a shell of carbonate of lime, the length of which is prolonged by each drop as it falls, till a stalactite is formed, varying in

* Solutions of the caustic alkalies, of alkaline carbonates, and arsenites, are also occasionally employed to prevent the formation of incrustations in boilers.

† From *σταλαζω, to drop; σταλαγμα, a drop.*

colour according to the nature of the substances which are separated from the water together with the carbonate of lime (such as the oxides of iron and vegetable matter); and as each drop falls from the point of the stalactite upon the floor of the cavern, it deposits there another shell of carbonate of lime, which grows, like the upper one, but in the opposite direction, and forms a stalagmite, thus adorning the grotto with conical pillars of carbonate of lime, sometimes, as in the case of the *oriental alabaster*, variegated with red and yellow, and applicable to ornamental purposes.

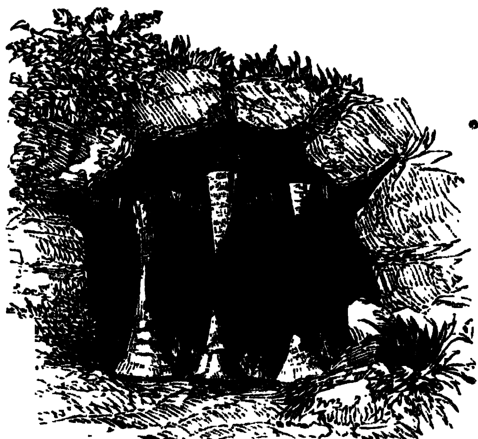


Fig. 45.—Stalactite cavern.

When water which has been boiled for some time is compared with unboiled water from the same source, it will be found to have become much softer, and this can now be easily explained, for, a considerable proportion of the salts of lime and magnesia having separated from the water, the latter is not capable of decomposing so large a quantity of soap. The amount of hardness which is thus destroyed by boiling is generally spoken of as *temporary* hardness, to distinguish it from the *permanent* hardness due to the soluble salts of lime and magnesia which still remain in the boiled water. It is customary with analytical chemists, in reporting upon the quality of natural waters, to express the hardness by a certain number of degrees which indicate the number of grains of chalk or carbonate of lime which would be dissolved in a gallon of water containing carbonic acid, in order to render its hardness equal to that of the water examined, that is, to render it capable of decomposing an equal quantity of soap. Thus, when a water is spoken of as having 16 degrees hardness, it is implied that 16 grs. of carbonate of lime dissolved in a gallon of water, containing carbonic acid, would render that gallon of water capable of decomposing as much soap as a gallon of the water under consideration.

The utility of a water for household purposes must be estimated, therefore, not merely according to the total number of degrees of hardness which it exhibits, but also by the proportion of that hardness which may be regarded as temporary, that is, which disappears when the water is boiled. Thus the total hardness of the New River water amounts to nearly 15 degrees, that of the Grand Junction Company to 14 degrees, and yet these waters are quite applicable to household uses, since their hardness is reduced by boiling to about 5 degrees. It has been ascertained that every degree of hardness in water gives rise to a waste of about 10 grs. of soap for every gallon of water employed, and hence the use of 100 gallons of Thames or New River water in washing will be attended with the loss of about 2 lbs. of soap; this loss is reduced, however, to about one-third when the temporary hardness has been destroyed by boiling.

The addition of washing soda (carbonate of soda) removes not only the temporary, but also the permanent hardness due to the presence of the sulphates of lime and magnesia in the water, for both these salts are decomposed by the carbonate of soda, which separates the lime and magnesia as insoluble carbonates, while sulphate of soda remains dissolved in the water.* The household practice of boiling the water, and adding a little washing soda, is therefore very efficacious in removing the hardness. *Clark's process* for softening waters depends upon the neutralisation of the free carbonic acid contained in the water by the addition of a certain quantity of lime; the lime thus added combines with the free carbonic acid, and the carbonate of lime so produced separates together with the carbonates of lime and magnesia, which were previously retained in solution by the free carbonic acid; this process, therefore, affects chiefly the temporary hardness; moreover, the earthy carbonates which are separated appear to remove from the water a portion of the organic matter which it contains, and thus effect a very important purification. The water under treatment is mixed, in large tanks, with a due proportion of lime previously diffused through water (the quantity necessary having been determined by preliminary experiment), and the mixture allowed to settle until perfectly clear, when it is drawn off into reservoirs.†

Waters which are turbid from the presence of clay in a state of suspension, are sometimes purified by the addition of a small quantity of alum or sulphate of alumina, when the alumina is precipitated by the carbonate of lime, and carries down with it mechanically the suspended clay, leaving the water clear.

The *organic matter* contained in waters may be vegetable matter dissolved from the earth, with which it has come in contact, or resulting from the decomposition of plants, or it may be animal matter derived either from the animalcules and fish naturally existing in it, or from the sewage of towns, and, in the case of well waters, from surface drainage. It is a pretty generally received opinion that such of these organic matters as are very susceptible of chemical change have an injurious effect upon the system of persons drinking the water, and it is now usual, in examining water as to its fitness for consumption, to ascertain how much of the organic matter is in a changeable condition, by determining with the aid of a solution of permanganate of potash the amount of oxygen necessary to effect its conversion into more stable forms.

It is believed, upon good medical authority, that cholera and diarrhœa are propagated by certain *spores* or *germs*, which are present in the evacuations of persons suffering from those maladies, and are conveyed into water which is allowed to become contaminated by sewage.

44. One of the most important points to be taken into account in estimating the qualities of a water is its action upon lead, since this metal is unfortunately so generally employed for the storage and transmission of water, and cases frequently occur in which the health has been seriously injured by repeated small doses of compounds of lead taken in water, which has been kept in a leaden cistern. If a piece of bright, freshly scraped lead be exposed to the air, it speedily becomes tarnished from the formation of a thin film of the oxide of lead, produced by the action of



* $CaO . SO_3 + Na_2O . CO_2 = Na_2O . SO_3 + CaO . CO_2$
Sulphate of lime. Carbonate of soda. Sulphate of soda. Carbonate of lime.

† Thames and New River water are softened, in this way, to 3°·5, or to a lower point than by an hour's boiling.

the atmospheric oxygen; this oxide of lead is soluble in water to some extent, and hence, when lead is kept in contact with water, the oxygen which is dissolved in it acts upon the metal, and the oxide so produced is dissolved by the water; but, fortunately, different waters act with very different degrees of rapidity upon the metal, according to the nature of the substances which they contain.

The film of oxide which forms upon the surface of the lead is insoluble, or nearly so, in water containing much sulphate or carbonate of lime, so that hard waters may generally be kept without danger in leaden cisterns; but soft waters, and those which contain nitrites or nitrates, should not be drunk after contact with lead. Nearly all waters which have been stored in leaden cisterns contain a trace of the metal, and since the action of this poison, in minute doses, upon the system is so gradual that the mischief is often referred to other causes, it is much to be desired that lead should be discarded altogether for the construction of cisterns.

Mineral waters, as they are popularly called, are simply spring waters containing so large a quantity of some ingredient as to have a decided medicinal action. They are differently named according to the nature of their predominating constituent. Thus, a *chalybeate* water contains a considerable quantity of a salt of the oxide of iron (usually the carbonate dissolved by free carbonic acid); an acidulous water is distinguished by a large proportion of carbonic acid, and is well exemplified in the celebrated Seltzer water; a sulphureous or hepatic water has the nauseous odour due to the presence of sulphuretted hydrogen. The Harrogate water is eminently sulphureous. Saline waters are such as contain a large quantity of some salt; thus the saline springs of Cheltenham are rich in common salt and sulphate of soda.

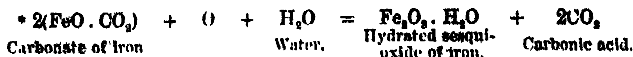
The chalybeate waters, which are by no means uncommon, become brown when exposed to the air, and deposit a rusty sediment which consists of the sesquioxide of iron, formed by the union of the oxygen of the air with the oxide of iron existing in the carbonate.*

45. *Sea water* contains the same salts as are found in waters from other natural sources, but is distinguished by the very large proportion of chloride of sodium (common salt). A gallon of sea water contains usually about 2500 grains of saline matter, of which 1890 grains consist of common salt. The circumstance that clothes wetted with sea water never become perfectly dry is to be ascribed chiefly to the *chloride of magnesium* present in the water, which is distinguished by its tendency to *deliquesce* or become damp in moist air. There are two elements, *bromine* and *iodine*, which are found combined with metals in appreciable quantity in sea water, though they are of somewhat rare occurrence in other waters derived from natural sources.

46. By *distillation*, pure water may be obtained from most spring and river waters.

(Definition.—*Distillation* is the conversion of a liquid into a vapour, and its recondensation into the liquid form in another vessel.)

Fig. 46 represents the ordinary form of still in common use, in which A is a copper boiler containing the water to be distilled; B the *head* of the still, which lifts out at *b*, and is connected by the neck C with the *worm* D, a tin pipe coiled round in the tub E, and issuing at F. The steam from the boiler, passing into the worm, is con-



* $2(FeO.CO_2) + O + H_2O = Fe_2O_3.H_2O + 2CO_2$

Carbonate of Iron. Water. Hydrated sesquioxide of iron. Carbonic acid.

densed to the liquid state, being cooled by the water in contact with the worm; this water, becoming heated, passes off through the pipe G, being replaced by cold water, which is allowed to enter through H.*

Another form of apparatus for distillation of water and other liquids is shown in fig. 47. A is a stoppered *retort*, the neck of which fits into the tube of a *Liebig's condenser* (B), which consists of a glass tube (C) fitted by means of corks into a glass, copper, or tinned iron tube (D), into which a stream of cold water is passed by the funnel E, the heated water running out through the upper tube F. The water furnished by the condensation of the steam passes through the *quilled receiver* G, into the flask H. Heat is gradually applied to the retort by a ring gas-burner.

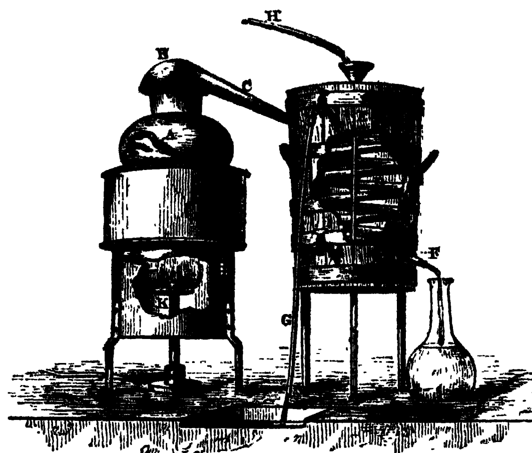


Fig. 46.

Many special precautions are requisite in order to obtain absolutely pure distilled water for refined experiments, but for ordinary purposes the common methods of distillation yield it in a sufficiently pure condition.

The saline matters present in the water are of course left behind in the still or retort. Sea water is now frequently distilled on board-ship when

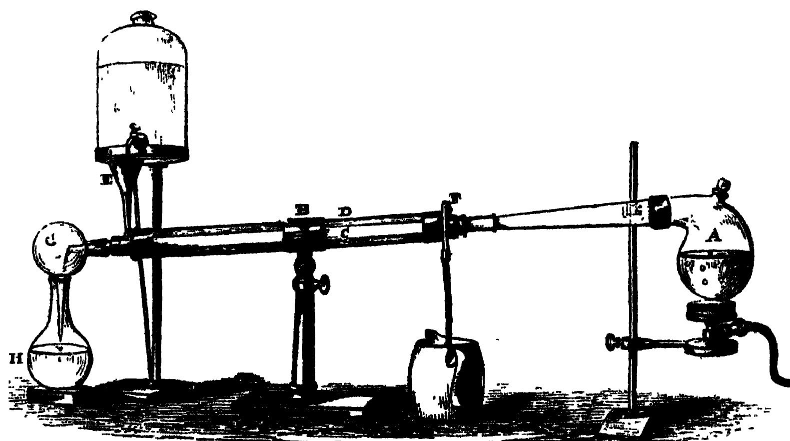


Fig. 47.—Distillation—Liebig's condenser.

fresh water is scarce. The vapid and disagreeable taste of distilled water, which is due to its having been deprived of the dissolved air during the distillation, is remedied by the use of Normandy's apparatus, which provides for the restoration of the expelled air.

* A rosette gas-burner (K) on Bunsen's principle is very convenient for a small still of this description.

47. The physical properties of water are too well known to require any detailed description. Its specific gravity in the liquid state is = 1, being taken as the standard to which the specific gravities of liquid and solid bodies are referred.

(DEFINITION.—The *specific gravity of a liquid or solid body* is its weight as compared with that of an equal volume of pure water at 60° F., 15°·5 C.)

Water assumes the solid form, under ordinary circumstances, at 32° F. (0° C.), and may be obtained in six-sided prismatic crystals. Snow consists of beautiful stellate groupings of these crystals. Ice has the specific gravity 0·9184. In the act of freezing, water expands very considerably, so that 174 volumes of water at 60° F. become 184 volumes of ice. The breakage of vessels, splitting of rocks, &c., by the congelation of water, are due to this expansion. Water passes off in vapour at all temperatures, the amount of vapour evolved in a given time of course increasing with the temperature. The boiling point of water is 212° F. (100° C.)

(DEFINITION.—The *boiling point* of a liquid is the constant temperature indicated by a thermometer, immersed in the boiling liquid in the presence of a coil of platinum wire, to facilitate disengagement of vapour, and at a pressure of 30 in. (762 mm.) Bar.)

At and above 212° F. at the ordinary atmospheric pressure (30 in. Bar.), water is an invisible vapour of specific gravity 0·622 (air = 1). One cubic inch of water at 60° F. becomes 1696 cubic inches of vapour at 212° F.

48. *Binoxide* or *peroxide of hydrogen* or *oxygenated water*, H_2O_2. This compound is not met with in nature, nor has it any important useful application in the arts. It has recently, however, acquired some importance as a medicinal agent, and it possesses very great interest for the student of chemical philosophy, because it helps to throw some light upon the atomic constitution of the elements.

To prepare the peroxide of hydrogen, some baryta (BaO) is heated in a current of oxygen, when it becomes converted into the peroxide of barium (BaO_2). If this be powdered, suspended in water, and acted upon by a stream of carbonic acid gas, the water becomes charged with the peroxide of hydrogen; $BaO_2 + H_2O + CO_2 = BaO.CO_2 + H_2O_2$. The carbonate of baryta is allowed to subside, and the clear solution of peroxide of hydrogen poured off.

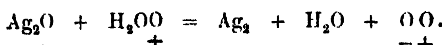
If a little powdered binoxide of manganese be thrown into the solution, brisk effervescence will ensue from the escape of oxygen, which may be recognised by the usual test with a partly extinguished match. The binoxide of manganese does not appear to be decomposed in this experiment, the whole of the oxygen being derived from the peroxide of hydrogen dissolved in the water, which is immediately decomposed, by contact with the binoxide of manganese, into water and free oxygen. If a solution of permanganate of potash be poured into a cylinder partly filled with the liquid, it will cause a rapid evolution of oxygen, derived not only from the peroxide of hydrogen, but from the permanganic acid, the red colour of which disappears, because it becomes reduced to a lower oxide of manganese.

The usual method of preparing peroxide of hydrogen in a pure state, consists in decomposing the peroxide of barium with diluted hydrochloric acid, under certain precautions to avoid the decomposition of the very unstable peroxide of hydrogen. Its formation is represented by the equation $BaO_2 + 2HCl = H_2O_2 + BaCl_2$. The chloride of barium is removed from the solution by the cautious addition of sulphate of silver, which precipitates the barium as sulphate of baryta, and the silver as chloride of silver, thus, $BaCl_2 + Ag_2O.SO_3 = 2AgCl + BaO.SO_3$. The precipitates are allowed to subside, and the clear liquid evaporated in the exhausted receiver of the air-pump over a dish of oil of vitriol to absorb the water, which evaporates much more rapidly than the peroxide. The pure peroxide of hydrogen is a syrupy liquid of sp. gr. 1·453, with a very slight chlorous odour. Its most remarkable feature is the facility with which it is decomposed into water and oxygen.* Even at 70° F.

* The presence of a little free acid renders it rather more stable, whilst free alkali has the opposite effect. A solution of peroxide of hydrogen, containing a little hydrochloric acid, is now sold for medicinal and photographic uses.

it begins to evolve bubbles of oxygen, so that it can scarcely be prepared in hot weather. At 212° it decomposes with violence. The mere contact with certain metals, such as gold, platinum, and silver, which have no direct attraction for oxygen, will cause the decomposition of the peroxide of hydrogen, without any chemical alteration of the metal itself.* It was noticed above that the binoxide of manganese decomposes it without undergoing any apparent change. The most surprising effect is that which takes place with oxide of silver. If a drop of peroxide of hydrogen be allowed to fall upon oxide of silver, which is a brown powder, decomposition takes place with explosive violence and great evolution of heat, the oxide of silver losing its oxygen, and becoming grey metallic silver. The oxides of gold and platinum are acted upon in a similar manner.

These very extraordinary changes, which were formerly described as *catalytic actions*, are now generally accounted for by the hypothesis that the oxygen in the oxide of silver, &c., exists in a condition different from that of the second atom of oxygen in the peroxide of hydrogen, and that these two conditions of oxygen have a chemical attraction for each other, similar to that which exists between different elements. If the oxygen in the oxide of silver be represented as *electro-negative* oxygen (see 5), as its relation to the metal would lead us to expect, and the second atom of oxygen in the peroxide of hydrogen be represented as *electro-positive* oxygen, the mutual decomposition of the two compounds might be represented by the equation,



$$\underset{-}{Ag_2O} + \underset{+}{H_2OO} = Ag_2 + H_2O + \underset{-+}{OO}.$$

This would support the conclusion arrived at by the train of reasoning at page 36, that the molecule or ultimate particle of free oxygen is really composed of two atoms.

49. OZONE.—This is the name given to a modified form of oxygen, of the true nature of which there is still some doubt, as it has never been obtained unmixed with ordinary oxygen, but it appears to be formed by the union of three atoms of oxygen (occupying three volumes), to produce a molecule of ozone (occupying two volumes). Just as peroxide of hydrogen (H_2O_2), may be regarded as formed by the combination of a molecule of water (H_2O) with an atom of oxygen, so ozone may be viewed as a combination of a molecule of oxygen (O_2) with an atom of oxygen. It would then be half as heavy again as ordinary oxygen, and experiment has shown that its rate of diffusion is in accordance with this view.

It derives its name from its peculiar odour (ὄζειν, *to smell*). Oxygen appears to be capable of assuming this *ozonised* condition under various circumstances, the principal of which are, the passage of silent electric discharges,† and the contact with substances (such as phosphorus) undergoing slow oxidation in the presence of water. A minute proportion of the oxygen obtained in the decomposition of water by the galvanic current also exists in the ozonised condition, as may be perceived by its odour.

The use of Siemens' induction tube (fig. 48) affords the readiest method of demonstrating the characteristic properties of ozone. This apparatus consists of a tube (A) coated internally with tin-foil (or silvered on the inside), and surrounded with another tube (B), which is coated with tin-foil on the outside. When the inner and outer coatings are placed in connexion with the wires of an induction coil by means of the screws (CD), and a stream of air or oxygen is passed through (E) between the two tubes, a strong odour is perceived at the orifice (F).

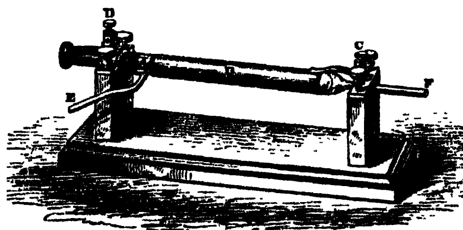


Fig. 48.—Tube for ozonising air by induction.

One of the best chemical tests for ozone is a damp mixture of starch with iodide

* Such inexplicable changes as this are sometimes included under the general denomination of *catalysis*, or decomposition by contact.

† It is the odour of ozone which is perceived in working an ordinary electrical machine.

of potassium. 100 grains of starch are well mixed in a mortar with a measured ounce of cold water, and the mixture is slowly poured into five ounces of boiling water in a porcelain dish, with occasional stirring. The thin starch-paste thus obtained is allowed to cool, and a few drops of solution of pure iodide of potassium are added, the mixture being well stirred with a glass rod. If this mixture be brushed over strips of white cartridge paper, these will remain unchanged in ordinary air; but when they are exposed to ozonised air (such as that which has passed through the induction tube), they will immediately assume a blue colour. The ozonised oxygen being more active, or endowed with more powerful chemical attractions than ordinary oxygen, abstracts the potassium from the iodide of potassium (KI), and sets free the iodine, which has the specific property of imparting a blue colour to starch. The intensity of the blue tint is proportionate to the quantity of iodine liberated, and therefore to that of the ozonised oxygen present, and hence, by reference to a standard scale of colours previously agreed upon, the ozone may be expressed in degrees. The result, however, is affected by so many trifling circumstances, that it is doubtful whether such determinations of the quantity of ozone are to be considered trustworthy. If the ozonised air issuing from F be passed into a solution of indigo (*sulphindigotic acid* largely diluted) the blue colour will soon disappear, since the ozone oxidises the indigo, and gives rise to products which, in a diluted state, are nearly colourless. Ordinary oxygen is incapable of bleaching indigo in this manner. If the ozone is passed through a tube of vulcanised caoutchouc, this will soon be perforated by the corrosive effect of the ozone, whilst ordinary oxygen would be without effect upon it.

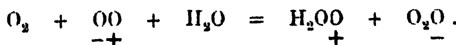
If the ozone from F be made to pass slowly through a glass tube heated in the centre by a spirit-lamp, it will be found to lose its power of affecting the iodised starch-paper, the ozone having been reconverted into ordinary oxygen under the influence of heat. A temperature of 300° F. is sufficient to effect this change. It has been observed that a given volume of oxygen diminishes when a portion of it is converted into ozone by the silent electric discharge, and that it regains its original volume when the ozone is reconverted by heat, proving that the ozonised form of oxygen is denser, or occupies less space than the ordinary form.

When a measured volume of pure oxygen was ozonised by the silent electric discharge until its volume had decreased by one-twelfth, and the ozone thus formed was absorbed by turpentine, it was found that two volumes of ozone had been produced from three volumes of oxygen.

On shaking the ozonised oxygen with mercury, the latter became partly converted into oxide, and the ozone disappeared, but there was no alteration in the volume of the oxygen, for (2 vols. ozone) $O_2O + Hg_2 = Hg_2O + O_2$ (2 vols.). Ozonised oxygen is deozonised when passed through a tube filled with binoxide of manganese, which also decomposes peroxide of hydrogen.

By placing a freshly-scraped stick of phosphorus (scraped under water to avoid inflammation) at the bottom of a quart bottle, with enough water to cover half of it, and loosely covering the bottle with a glass plate, enough ozone may be accumulated in a few minutes to be readily recognised by the odour and the iodised starch.

The water at the bottom of the bottle is found to contain, besides the phosphorous acid formed by the slow oxidation of the phosphorus, some peroxide of hydrogen, whence it has been supposed that the formation of ozone is due to the decomposition of a molecule of oxygen into electro-negative oxygen, which combines with another molecule of oxygen to form ozone, and electro-positive oxygen, which combines with a molecule of water to form peroxide of hydrogen. Thus,



$$O_2 + \underset{-\,+}{OO} + H_2O = H_2\underset{+}{O}O + O_2\underset{-}{O}.$$

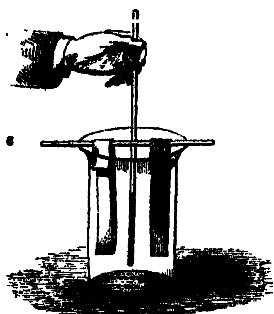
This view is supported by the circumstance, that peroxide of hydrogen appears to be produced in every case where ozone is formed in the presence of water.

If a few drops of ether be poured into a quart beaker (fig. 49), taking care to avoid the vicinity of a flame, and pieces of iodised starch-paper and blue litmus paper be suspended upon a glass rod laid across the mouth of the beaker, they will be found unaffected by the mixture of ether vapour and air; but if a hot glass rod be plunged into the beaker, the heated ether vapour will undergo oxidation, producing acid vapours, which redden the blue litmus, whilst the formation of ozone will be indicated by the blue iodised starch.*

Ether and essential oils, such as turpentine, slowly absorb oxygen from the air,

* The oxygen obtained by the action of warm sulphuric acid on binoxide of barium resembles ozone in its odour and action on the iodised starch-paper.

thus acquiring the property of bleaching indigo and of bluing the mixture of iodide of potassium and starch; hence they were formerly believed to contain ozone, but they do not answer to all the tests for that substance. Thus, ozone imparts a blue colour to the resin of *guaiacum*, but the old turpentine or ether will not do so. If a little peroxide of hydrogen be dissolved in ether, it exhibits the same property as the ether which has absorbed oxygen from the air, and it is, therefore, sometimes called "*ozonic ether.*" The solution of peroxide of hydrogen in ether (obtained by shaking the aqueous solution of the peroxide with ether) is employed by Dr Day for the recognition of blood-stains. Contact with blood decomposes peroxide of hydrogen, and the oxygen which is liberated is capable of bluing guaiacum resin. Accordingly, if a blood-stain be moistened with tincture of guaiacum (a solution of the resin in spirit of wine), and afterwards with the ethereal solution of peroxide of hydrogen (ozonic ether), it acquires an intense blue colour, which may be detected, even on a coloured fabric, by pressing a piece of white blotting-paper upon it.


Fig. 49.

Ozone has attracted much notice, because a minute proportion of the oxygen in the atmosphere appears sometimes to be present in this form, and its active properties have naturally led to the belief that it must exercise some influence upon the sanitary condition of the air This idea is encouraged by the circumstance that no indications of ozone can be perceived in crowded cities, where there are so many oxidisable substances to consume the active oxygen, whilst the air in the open country and at the sea-side does give evidence of its presence. Some chemists assert that their experiments have demonstrated the very important fact that a portion of the oxygen developed by growing plants is in the ozonised form.

ATMOSPHERIC AIR.

50. Atmospheric air consists chiefly of a mixture of nitrogen with one-fifth of its volume of oxygen, and very small proportions of carbonic acid and ammonia. Vapour of water is of course always present in the atmosphere in varying proportions. Since the atmosphere is the receptacle for all gaseous emanations, other substances may be discovered in it by very minute analysis, but in proportions too small to have any perceptible influence upon its properties. Thus marsh-gas or light carburetted hydrogen, sulphuretted hydrogen, and sulphurous acid, can often be traced in it, the two last especially in or near towns.

Although the proportion of oxygen in the air at a given spot may be much diminished, and that of carbonic acid increased, by processes of oxidation (such as respiration and combustion) taking place there, the operation of wind and of diffusion so rapidly mixes the altered air with the immensely greater general mass of the atmosphere, that the variations in the composition of air in different places are very slight. Thus it has been found that the proportion of oxygen in the air in the centre of Manchester was, at most, only 0·2 per cent. below the average.

The proportions in which the oxygen and nitrogen are generally present in atmospheric air are—

	Volumes.	Weights.
Nitrogen, ...	79·19	76·99
Oxygen, ...	20·81	23·01
	100·00	100·00

The proportion of aqueous vapour may be stated, on the average, as 1·4 per cent. by volume, or 0·87 per cent. by weight of the air. The carbonic acid may be generally estimated at 0·04 per cent. by volume, or 0·06 per cent. by weight of the air.

The relative proportions of oxygen and nitrogen in air may be exhibited by suspending a stick of phosphorus upon a wire stand (A, fig. 50) in a measured volume of air confined over water. The cylinder (B) should have been previously divided into five equal spaces by measuring water into it, and marking each space by a thin line of Brunswick black. After a few hours, the phosphorus will have combined with the whole of the oxygen to form phosphorous acid, which is absorbed by the water, leaving four of the spaces occupied by nitrogen.

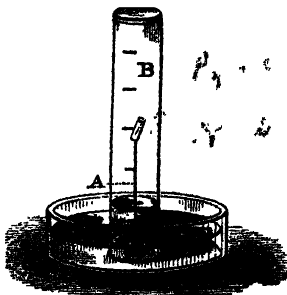


Fig. 50.

The same result may be arrived at in a much shorter time by burning the phosphorus in the confined portion of air.

A fragment of phosphorus, dried by careful pressure between blotting paper, is placed upon a convenient stand (A, fig. 51) and covered with a tall jar, having an opening at the top for the insertion of a well-fitting stopper (which should be greased with a little lard), and divided into seven parts of equal capacity. The jar should be placed over the stand in such a manner that the water may occupy the two lowest spaces into which the jar is divided. The stopper of the jar is furnished with a hook, to which a piece of brass chain (B) is attached, long enough to touch the phosphorus when the stopper is inserted. The end of this chain is heated in the flame of a lamp, and the stopper tightly fixed in its place. On allowing the hot chain to touch the phosphorus, it bursts into vivid combustion, filling the jar with thick white fumes, and covering its sides, for a few moments, with white flakes of phosphoric acid. At the commencement of the experiment, the water in the jar will be depressed, in consequence of the expansion of the air, due to the heat produced in the burning of the phosphorus, but, presently, when the combustion begins to decline, the water again rises, and continues to do so until it has ascended to the line (C), so as to occupy the place of one-fifth of the air employed in the experiment. The phosphorus will then have ceased to burn, the white flakes upon the sides of the jar will have acquired the appearance of drops of moisture, and the fumes will have gradually disappeared, until, in the course of half-an-hour, the air remaining in the jar will be as clear and transparent as before, the whole of the phosphoric acid having been absorbed by the water. The jar should now be sunk in water, so that the latter may attain to the same level without as within the jar. On removing the stopper, it will be found that the nitrogen in the jar will no longer support the combustion of a taper.

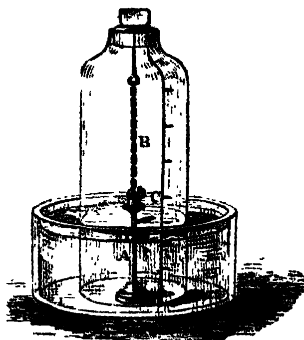


Fig. 51.

In the rigidly accurate determination of the relative proportions of oxygen and nitrogen in the air, it is, of course, necessary to guard against any error arising from the presence of the water, carbonic acid, and ammonia. With this view, Dumas and Boussingault, to whom we are chiefly indebted for our exact knowledge of the composition of the air, caused it to pass through a series of tubes (A, fig. 52) containing potash, in order to remove the carbonic acid, then through a second series (B), containing sulphuric acid, to absorb the ammonia and water; the purified air then passed through a glass tube (C) filled with bright copper heated to redness in a charcoal furnace, which removed the whole of the oxygen, and the nitrogen passed into the large globe (N).

Both the tube (containing the copper) and the globe were carefully exhausted of air and accurately weighed before the experiment; on connecting the globe and the tube with the purifying apparatus, and slowly opening the stop-cocks, the pressure of the external air caused it to flow through the series of tubes into the globe destined

to receive the nitrogen. When a considerable quantity of air had passed in, the stop-cocks were again closed, and, after cooling, the weight of the globe was accurately determined. The difference between this weight and that of the empty globe before the experiment, gave the weight of the nitrogen which had entered the globe, but this did not represent the whole of the nitrogen contained in the analysed air, for the

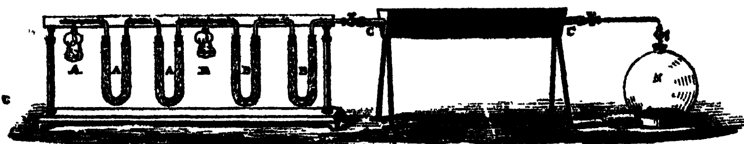


Fig. 52. –Exact analysis of air.

tube containing the copper had, of course, remained full of nitrogen at the close of the experiment. This tube having been weighed, was attached to the air-pump, the nitrogen exhausted from it, and the tube again weighed; the difference between the two weighings furnished the weight of the nitrogen remaining in the tube, and was added to the weight of that received in the globe. The oxygen was represented by the increase in the weight of the exhausted tube containing the copper, which was partially converted into oxide of copper, by combining with the oxygen of the air passed through it.

The calculation of the result of the analysis is here exemplified :—

Weight of	Grains	
Globe (N) with nitrogen (at the conclusion), ...	3076	
Exhausted globe (at the commencement), ...	3000	
Nitrogen received into the globe, ...	76	
Tube (C) with residual nitrogen (at the conclusion), .	2574	
Exhausted tube (at the conclusion), ...	2573	
Nitrogen remaining in the tube, ...	1	
Add nitrogen received into the globe, . .	76	
Total nitrogen in the air analysed, . .	77	
Exhausted tube (C) with oxidised copper (at the conclusion), .		2573
,, ,, metallic copper (at the commencement),		2550
Oxygen in the air analysed, ...		23

The ratio of the nitrogen to the oxygen, therefore, is that of 23 N : 77 O, or 1 N : 3·347 O. 100 parts by weight of the air purified from water, carbonic acid, and ammonia, contain 77 parts of nitrogen and 23 parts of oxygen.

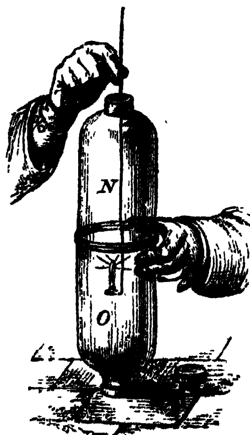


Fig. 53.

51. The nitrogen remaining after the removal of the oxygen from air in the above experiments was so called on account of its presence in nitre (saltpetre KNO_3). In physical properties it resembles oxygen, but is somewhat lighter than that gas, its specific gravity being 0·9713.

This difference in the specific gravities of the two gases is well exhibited by the arrangement shown in fig. 53. A jar of oxygen (O) is closed with a glass plate, and placed upon the table. A jar of nitrogen (N), also closed with a glass plate, is placed over it, so that the two gases may come in contact when the glass plates are removed. The nitrogen will float for some seconds above the oxygen, and if a lighted taper be quickly introduced through the neck of the upper jar, it will be extinguished in passing through the nitrogen, and will be rekindled brilliantly when it reaches the oxygen in the lower jar.

It might at first sight appear surprising that oxygen and nitrogen, though of different specific gravities, should exist in uniform proportions in all parts of the atmosphere, unless in a state of chemical combination; but an acquaintance with the property of diffusion (see 13) possessed by gases teaches us that *gases will mix with each other in opposition to gravitation, and when mixed will always remain so.*

It was shown by Graham that a partial separation of the nitrogen and oxygen in air may be effected, on the same principle as that of hydrogen and oxygen at page 18, by taking advantage of the difference in their rates of diffusion. He devised, however, a more convenient process, founded upon the *dialytic* passage of the gases through caoutchouc, which he ascribed to the absorption of the gas by the solid material upon one side, and its escape on the other.

A bag (*a*, fig. 54) is made of a fabric composed of a layer of caoutchouc between two layers of silk, such as that employed for waterproof garments; a piece of carpet is placed inside the bag to keep the sides apart, and the edges of the bag are made perfectly air-tight with solution of caoutchouc. To maintain a vacuum within the bag, it is supported by the rod *v*, and attached to *Sprengel's air-pump*, in which a stream of mercury, allowed to flow from a funnel (*f*) down a tube (*c*) six feet long, draws the air out of the bag, through a lateral tube (*h*), until all the air is exhausted, which is indicated by the barometer tube *b*, the lower end of which dips into a cistern of mercury. When the mercury in this tube stands at almost exactly the same height as the standard barometer, the exhaustion is complete. If a test-tube (*d*) filled with mercury be now inverted over the end of the long tube *c*, which is bent upwards for that purpose, the bubbles of air which are drawn through the sides of the vacuous bag, and carried down the long tube by the little pistons of liquid mercury as they fall, will pass up into the test-tube; when the latter is filled with the gas, its mouth is closed with the thumb, withdrawn from the mercury, and a match with a spark at the end inserted, when the spark will burst out into flame, showing that the specimen of air collected is much richer in oxygen than ordinary atmospheric air. The overflow tube *g* delivers the mercury which is to be returned to the funnel *f*.

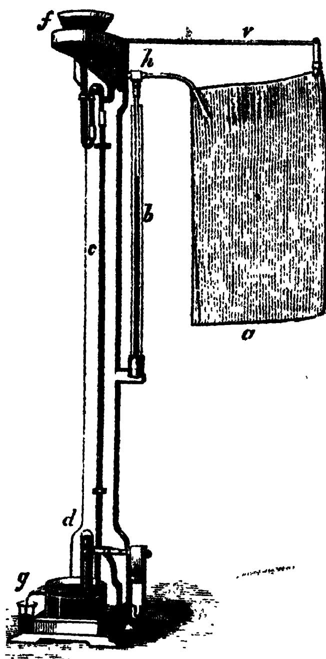


Fig 54.– Sprengel's pump. Dialysis of air.

The dialytic passage of oxygen through caoutchouc into a vacuum is twice as rapid as that of nitrogen, so that the air collected in the tube contains twice as much oxygen as the external air.

This dialytic passage of gases through solids is quite unconnected with the diffusibility of the gases, and appears to depend rather upon the chemical nature of the gas and of the solid. It is thus connected with the *occlusion* of gases by solids, exemplified in the case of palladium and hydrogen at page 38. It is in consequence of this dialytic passage that tubes of iron or platinum, which are quite impermeable by hydrogen at the ordinary temperature, will allow it to pass rapidly through their walls at high temperatures.

That air is simply a mechanical mixture of its component gases is amply proved by the circumstance that it possesses all the properties which would be predicted for a *mixture* of these gases in such proportions; whilst the essential feature of a *chemical compound* is, that its properties cannot be foreseen from those of its constituents.

The absence of active chemical properties is a very striking feature of nitrogen, and admirably adapts it for its function of diluting the oxygen in the atmosphere.

The chemical relations of air to animals and plants will be more appropriately discussed hereafter. (See *Carbonic Acid*, *Ammonia*.)

CARBON.

C = 12 parts by weight.*

52. This element is especially remarkable for its uniform presence in organic substances. The ordinary laboratory test by which the chemist decides whether a substance under examination is of organic origin, consists in heating it with limited access of air, and observing whether any blackening from separation of carbon (*carbonisation*) ensues.

Few elements are capable of assuming so many different aspects as carbon. It is met with transparent and colourless in the *diamond*, opaque, black, and quasi-metallic in *graphite* or black lead, velvety and porous in wood-*charcoal*, and under new conditions in *anthracite*, *coke*, and *gas-carbon*.

In nature, free carbon may be said to occur in the forms of diamond, graphite, and anthracite (the other varieties of coal containing considerable proportions of other elements).

Apart from its great beauty and rarity, the diamond possesses a special interest in chemical eyes, from its having perplexed philosophers up to the middle of the last century, notwithstanding the simplicity of the experiments required to demonstrate its true nature. The first inkling of it appears to have been obtained by Newton, when he perceived its great power of refracting light, and thence inferred that, like other bodies possessing that property in a high degree, it would prove to be combustible ("an unctuous substance coagulated"). When this prediction was verified, the burning of diamonds was exhibited as a marvellous experiment, but no accurate observations appear to have been made till 1772, when Lavoisier ascertained, by burning diamonds suspended in the focus of a burning-glass, in a confined portion of oxygen, that they were entirely converted into carbonic acid gas. In more recent times this experiment has been repeated with the utmost precaution, and the diamond has been clearly demonstrated to consist of carbon in a crystallised state.

A still more important result of this experiment was the exact determination of the composition of carbonic acid, without which it would not be possible to ascertain exactly the proportion of carbon in any of its numerous compounds, since it is always weighed in that form.

The most accurate experiments upon the synthesis of carbonic acid have been conducted with the arrangement represented in fig. 55.

Within the procelain tube A, which is heated to redness in a charcoal fire, was placed a little platinum tray, accurately weighed, and containing a weighed quantity of fragments of diamond. One end of the tube was connected with a gas-holder B, containing oxygen which was thoroughly purified by passing through the tube C, containing potash (to absorb any carbonic acid and chlorine which it might contain), and dried by passing over pumice soaked with concentrated sulphuric acid in D and E. To the other end of the porcelain tube A, there was attached a glass tube F, also heated in a furnace, and containing oxide of copper, to convert into carbonic

* The volume occupied by carbon in the form of vapour is not known, its vapour never having been obtained in a measurable form.

acid any carbonic oxide which might have been formed in the combustion of the diamond. The carbonic acid was then passed over pumice soaked with sulphuric acid in G, to remove any traces of moisture, and afterwards into a weighed bulb-apparatus H, containing solution of potash, and two weighed tubes I, K, containing,

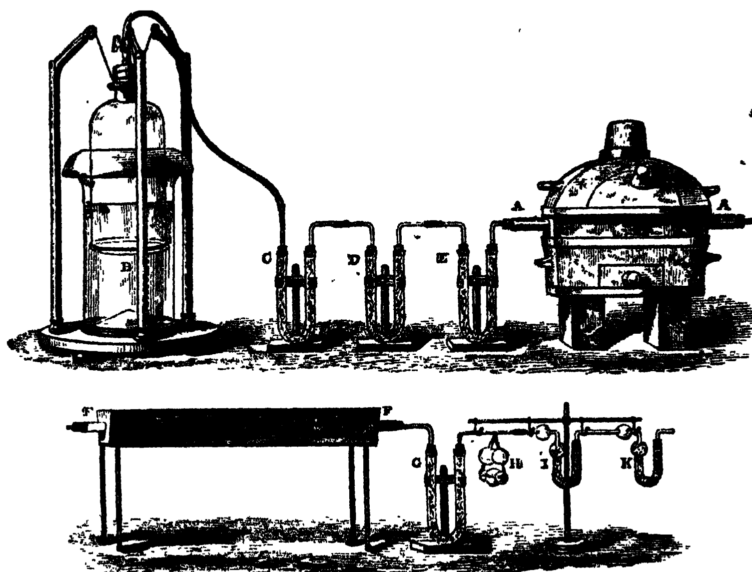


Fig. 55.—Exact synthesis of carbonic acid.

respectively, solid hydrate of potash, and sulphuric acid on pumice, to guard against the escape of aqueous vapour taken up by the excess of oxygen in its passage through the bulbs H. The increase of weight in H, I, K, represented the carbonic acid formed in the combustion of an amount of diamond indicated by the loss of weight suffered by the platinum tray, and the difference between the diamond consumed and the carbonic acid formed would express the amount of oxygen which had

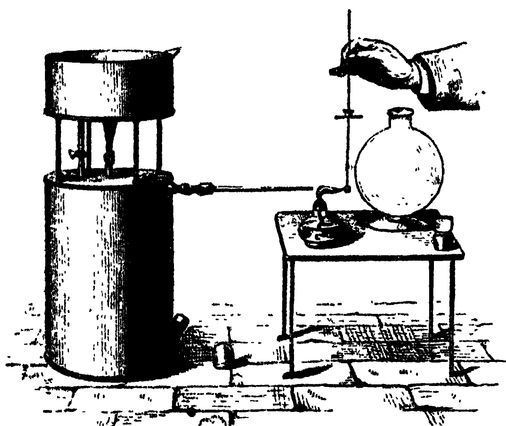


Fig. 56.

combined with the carbon. A large number of experiments conducted in this manner, both with diamond and graphite, showed that 12 parts of carbon furnished 44 parts of carbonic acid, and consumed, therefore, 32 parts of oxygen.

The ordinary mode of exhibiting the combustion of the diamond on the lecture

table, consists in suspending it within a double loop of platinum wire attached to an iron wire passing through a deflagrating-collar, and heating it in a jet of oxygen sent through a gas or spirit flame (fig. 56). As soon as it has attained a white heat, the diamond is plunged into a globe of oxygen, and after burning for a few seconds, it is withdrawn, and a little lime-water is shaken in the globe to produce the milky deposit of carbonate of lime. It not unfrequently happens that the blowpipe flame fuses the platinum wire, and the diamond drops out before it can be immersed in the oxygen. A more convenient arrangement is shown in fig. 57. The diamond is supported in a short helix of platinum wire A, which is attached to the copper wires B B, passing through the cork C, and connected with the terminal wires of a Grove's battery of five or six cells. The globe having been filled with oxygen by passing the gas down into it till a match indicates that the excess of oxygen is streaming out of the globe, the cork is inserted, and the wires connected with the battery. When the heat developed in the platinum coil, by the passage of the current, has raised the diamond to a full red heat, the connexion with the battery may be interrupted, and the diamond will continue to burn with steady and intense brilliancy.

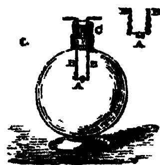


Fig. 57.

To an observer unacquainted with the satisfactory nature of this demonstration, it would appear incredible that the transparent diamond, so resplendent as to have been reputed to emit light, should be identical in its chemical composition with graphite (*plumbago* or *black lead*) from which, in external appearance, it differs so widely. For this difference is not confined to their colour; in crystalline form they are not in the least alike, the diamond occurring generally in octahedral crystals, while graphite is found either in *amorphous* masses (that is, having no definite crystalline form), or in six-sided plates which are not geometrically allied with the form assumed by the diamond. Carbon, therefore, is *dimorphous*, or occurs in two distinct crystalline forms. Even in weight, diamond and graphite are very dissimilar, the former having an average specific gravity of 3·5, and the latter of 2·3. Again, a crystal of diamond is the hardest of all substances, whence it is used for cutting and for writing upon glass, but a mass of graphite is soft and easily cut with a knife. The diamond is a non-conductor of electricity, but the conducting power of graphite renders it useful in the electrotype process.

Diamonds are chiefly obtained from Golconda, Borneo, and the Brazils. They usually occur in sandstone rock or in mica slate. The hardness of the diamond renders it necessary to employ diamond-dust for the purpose of cutting and polishing it, which is effected with the aid of a revolving disk of steel, to the surface of which the diamond-dust is applied in the form of a paste made with oil. The crystal in its natural state is best fitted for the purpose of the glazier, for its edges are usually somewhat curved, and the angle formed by these cuts the glass deeply, while the angle formed by straight edges, like those of an ordinary jeweller's diamond, is only adapted for scratching or writing upon glass. Drills with diamond points have been employed in tunnelling through hard rocks. The diamond-dust used for polishing, &c., is obtained from a dark amorphous diamond found at Bahia in the Brazils; 1000 ounces annually are said to have been occasionally obtained from this source. When burnt, the diamond always leaves a minute proportion of ash of a yellowish colour in which silica and oxide of iron have been detected. A genuine diamond may be known by its combining the three qualities of extreme hardness, enabling it to scratch hardened steel, high specific gravity (3·53), and insolubility in hydrofluoric acid.

Although the diamond, when preserved from contact with the air, may

be heated very strongly in a furnace, without suffering any change, it is not proof against the intense heat of the discharge taking place between two carbon points attached to the terminal wires of a powerful galvanic battery. If the experiment be performed in a vessel exhausted of air, the diamond becomes converted into a black coke-like mass which closely resembles graphite in its properties.

Graphite always leaves more ash than the diamond, consisting chiefly of the oxides of iron and manganese, with particles of quartz, and sometimes titanic acid. The purest specimens are those of compact amorphous graphite from Borrowdale in Cumberland; an inferior variety, imported from Ceylon, is crystalline, being composed of hexagonal plates. Graphite is obtained artificially in the manufacture of cast iron: in some cases, a portion of the carbon of the cast iron separates in cooling, in the form of crystalline scales of graphite, technically called *kish*. In the grey variety of cast iron these scales of graphite are diffused through the mass of the metal, and are left undissolved when the iron is dissolved by an acid.

Graphite is far more useful than the diamond, for, in addition to its application in black lead pencils, and for covering the surface of iron in order to protect it from rust, it is largely employed, in admixture with clay, for the fabrication of the black lead crucibles or *blue pots*, as they are commonly called, which are so valuable to the metallurgist, for their power of resisting high temperatures. Graphite is also sometimes employed for lubricating, to diminish friction in machinery, and for *facing* or imparting a fine glazed surface to gunpowder.

(Anthracite and the other varieties of coal will be described in a separate section.)

53. Several varieties of carbon, obtained by artificial processes, are employed in the arts. The most important of these are *lamp black*, *wood charcoal* and *animal charcoal*.

Lamp black approaches more nearly in composition to pure carbon than either of the others, and is the soot obtained from the imperfect combustion of resinous and tarry matters (or of highly bituminous coal), from which source it derives the small quantities of resin, of nitrogen, and sulphur which it contains. The uses of this substance, as an ingredient of pigments, of printing ink, and of blacking, depend evidently more upon its black colour than upon its chemical properties.

Wood charcoal presents more features which arrest the attention of the chemist, as well on account of its specific properties, as of the influence exercised by the method adopted for obtaining it, upon its fitness for the particular purpose which it may be destined to serve.

If a piece of wood be heated in an ordinary fire, it is speedily consumed, with the exception of a grey ash consisting of the incombustible mineral substances which it contained; if the experiment were performed in such a manner that the products of combustion of the wood could be collected, these would be found to consist of carbonic acid and water; woody fibre is composed of carbon, hydrogen, and oxygen ($C_6H_{10}O_5$), and when it is burnt, the oxygen, in conjunction with more oxygen derived from the air, converts the carbon and hydrogen into carbonic acid and water. But if the wood be heated in a glass tube, closed at one end, it will be found impossible to reduce it, as before, to an ash, for a mass of charcoal will remain, having the same form as that of the piece of wood;

in this case, the oxygen of the air not having been allowed free access to the wood, no true combustion has taken place, but the wood has undergone *destructive distillation*, that is, its elements have arranged themselves, under the influence of the high temperature, into different forms of combination, for the most part simpler in their chemical composition than the wood itself, and capable, unlike the wood, of enduring that temperature without decomposition; thus, it is merely an exchange of an unstable for a stable equilibrium of the particles of matter composing the wood.

(DEF.—*Destructive distillation* is the resolution of a complex substance into simpler forms under the influence of heat, out of contact with air.)

The vapours issuing from the mouth of the tube will be found acid to blue litmus paper; they have a peculiar odour, and readily take fire on contact with flame. These will be more particularly noticed hereafter, as they contain some very useful substances. The charcoal which is left is not pure carbon, but contains considerable quantities of oxygen and hydrogen, with a little nitrogen, and the mineral matter or ash of the wood.

When the charcoal is to be used for fuel, it is generally prepared by a process in which the heat developed by the combustion of a portion of the wood is made to effect the charring of the rest. With this view the billets of wood are built up into a heap (fig. 58) around stakes driven into the ground, a passage being left so that the heap may be kindled in the centre. This mound of wood, which is generally from 30 to 40 feet in diameter, is closely covered with turf and sand, except for a few inches around the base, where it is left uncovered to give vent to the vapour of water expelled from the wood in the first stage of the process.

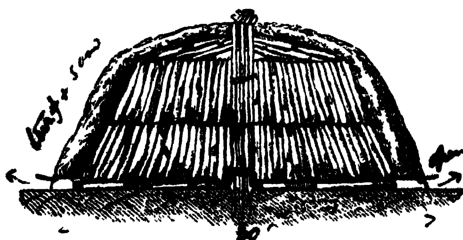


Fig. 58.—Charcoal heap.

When the heap has been kindled in the centre, the passage left for this purpose is carefully closed up. After the combustion has proceeded for some time, and it is judged that the wood is perfectly dried, the open space at the base is also closed, and the heap left to smoulder for three or four weeks, when the wood is perfectly carbonised.

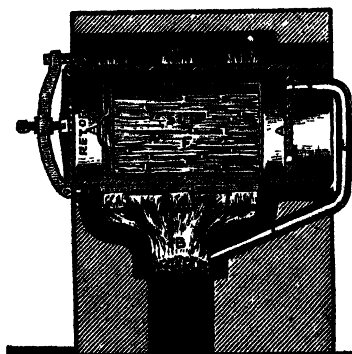


Fig. 59.—Charcoal retort.

Upon an average, 22 parts of charcoal are obtained by this process from 100 of wood.

A far more economical process for preparing charcoal from wood consists in heating it in an iron case or *slip* (F, fig. 59) placed in an iron retort A, from which the gases and vapours are conducted by the pipe L into the furnace B, where they are consumed.

On the small scale, the operation may be conducted in a glass

retort, as shown in fig. 60, where the water, tar, and naphtha are deposited in the globular receiver, and the inflammable gases are collected over water.

The infusibility of the charcoal left by wood accounts for its very great porosity, upon which some of its most remarkable and useful properties depend. The application of charcoal for the purpose of "sweetening" fish and other food in a state of incipient putrefaction has long been practised, and more recently charcoal has been employed for *deodorising* all kinds of putrefying and offensive animal or vegetable matter. This property of charcoal depends upon its power of absorbing into its pores very considerable quantities of the gases, especially of those which are easily absorbed by water. Thus, one cubic inch of charcoal is capable of absorbing about 100 cubic inches of ammonia gas and 50 cubic inches of sulphuretted hydrogen, both which are conspicuous among the offensive results of putrefaction. This condensation of gases by charcoal is a mechanical effect, and does not involve a chemical combination of the charcoal with the gas; it is exhibited most powerfully by charcoal which has been recently heated to redness in a closed vessel, and cooled out of contact with air by plunging it under mercury. Eventually the offensive gases absorbed by the charcoal are chemically acted on by the oxygen of the air in its pores. A cubic inch of wood charcoal absorbs nearly 10 cubic inches of oxygen, and when the charcoal containing the gas thus condensed is presented to another gas which is capable of undergoing oxidation, this latter gas is oxidised and converted into inodorous products. Thus, if charcoal be exposed to the action of air containing sulphuretted hydrogen gas, it condenses within its pores both this gas and

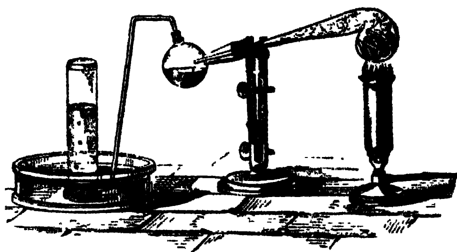


Fig. 60.—Distillation of wood.

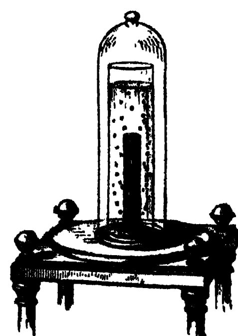


Fig. 61.

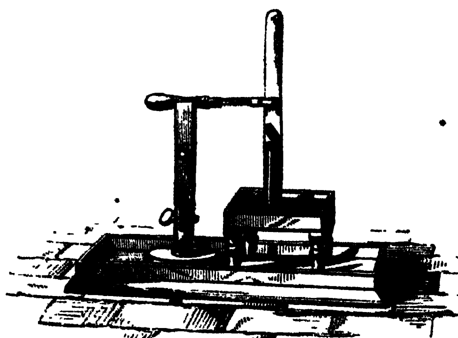


Fig. 62.

the atmospheric oxygen, which then converts the hydrogen into water (H_2O) and the sulphur into sulphuric acid (SO_3).

The great porosity of wood charcoal is strikingly exhibited by attaching a piece of lead to a stick of charcoal (fig. 61), so as to sink it in a cylinder of water, which is

then placed under the receiver of the air-pump. On exhausting the air, innumerable bubbles will start from the pores of the charcoal, causing brisk effervescence. If a glass tube 16 or 18 inches long be thoroughly filled with ammonia gas (fig. 62), supported in a trough containing mercury, and a small stick of recently calcined charcoal introduced through the mercury into the tube, the charcoal will absorb the ammonia so rapidly that the mercury will soon be forced up and fill the tube, carrying the charcoal up with it. On removing the charcoal, and placing it upon the hand, a sensation of cold will be perceived from the rapid escape of ammonia, perceptible by its odour.

By exposing a fragment of recently calcined wood-charcoal under a jar filled with hydrosulphuric acid gas for a few minutes, so that it may become saturated with the gas, and then covering it with a jar of oxygen, the latter gas will act upon the former with such energy that the charcoal will burst into vivid combustion. The jar must not be closed air-tight at the bottom, or the sudden expansion may burst it. Charcoal in powder exposed in a porcelain crucible may also be employed in the same way. It should be pretty strongly heated in the covered crucible, and allowed to become nearly cool before being exposed to the hydrosulphuric acid.

Charcoal prepared from hard woods absorbs the largest volume of gas. Thus logwood charcoal has been found to absorb 111 times its volume of ammoniacal gas. Charcoal made from the shell of the cocoa-nut is even more absorbent, although its pores are quite invisible, and its fracture exhibits a semi-metallic lustre.

As the gases which are evolved in putrefaction are of a poisonous character, the power of wood charcoal to remove them acquires great practical importance, and is applied in very many cases; the charcoal in coarse powder is thickly strewn over matters from which the effluvium proceeds, or is exposed in shallow trays to the air to be sweetened, as in the wards of hospitals, &c. It has even been placed in a flat box of wire gauze to be fixed as a ventilator before a window through which the contaminated air might have access, and respirators constructed on the same principle have been found to afford protection against poisonous gases and vapours. The ventilating openings of sewers in the streets are also fitted with cases containing charcoal for the same purpose. Water is often filtered through charcoal in order to free it from the noxious and putrescent organic matters which it sometimes contains. For all such uses the charcoal should have been recently heated to redness in a covered vessel in order to expel the moisture which it attracts when exposed to the air; and the charcoal which has lost its power of absorption will be found to regain it in great measure when heated to redness.



Fig. 63.—Filtration.

This power of absorption which charcoal possesses is not confined to gases, for many liquid and solid substances are capable of being removed by that agent from their solution in water. This is most readily traced in the case of substances which impart a colour to the solution, such colour being often removed by the charcoal; if port wine or infusion of logwood be shaken with powdered charcoal (especially if the latter has been recently heated to redness in a closed crucible), the liquid, when filtered through blotting paper (fig. 63), will be found to have lost its colour; the colouring matter, however, seems merely to have adhered to the charcoal, for it may be extracted from the latter by treatment with a weak alkaline liquid.

The *decolorising power* of wood charcoal is very feeble in comparison with that possessed by *bone-black* or *animal charcoal*, which is obtained by heating bones in vessels from which the air is excluded. Bones are composed of about one-third of animal and two-thirds of mineral substances, the latter including phosphate of lime, which amounts to more than half the weight of the bone, and a little carbonate of lime. When bone is heated, as in a retort, so that air is not allowed to have free access to it, the animal matter undergoes destructive distillation, its elements—carbon, hydrogen, nitrogen, and oxygen—assuming other forms, the greater part of the three last elements, together with a portion of the carbon, escaping in different gaseous and vaporous products, while a considerable proportion of the carbon remains behind, intimately mixed with the earthy ingredients of the bone, and constituting the substance known as animal charcoal. The great difference between the products of the destructive distillation of bone and of wood deserves a passing notice. If a fragment of bone or a shaving of horn be heated in a glass tube closed at one end, the vapours which are evolved will be found strongly *alkaline* to test-papers, while those furnished by the wood were *acid*; this difference is to be ascribed mainly to the presence of nitrogen in the bone, wood being nearly free from that element; it will be found to hold good as a general rule, that the results of the destructive distillation of animal and vegetable matters containing much nitrogen are alkaline, from the presence of ammonia (NH_3) and similar compounds, while those furnished by non-nitrogenised substances possess acid characters: the peculiar odour which is emitted by the heated bone is characteristic, and affords us a test by which to distinguish roughly between nitrogenised and non-nitrogenised bodies.

An examination of the charred mass remaining as the ultimate result of the action of heat upon bone, shows it to contain much less carbon than that furnished by wood, for the bone-charcoal contains nearly nine-tenths of its weight of phosphate (with a little carbonate) of lime; the consequence of the presence of so large an amount of earthy matter must be to extend the particles of carbon over a larger space, and thus to expose a greater surface for the adhesion of colouring matters, &c. This may partly help to explain the very great superiority of bone-black to wood charcoal as a decolorising agent, and the explanation derives support from the circumstance, that when animal charcoal is deprived of its earthy matter, for chemical uses, by washing with hydrochloric acid, its decolorising power is very considerably reduced. The application of this variety of charcoal is not confined to the chemical laboratory, but extends to manufacturing processes. The sugar-refiner decolorises his syrup by filtering it through a layer of animal charcoal, and the distiller employs charcoal to remove the empyreumatic oils with which distilled spirits are frequently contaminated.

Carbon is remarkable, among elementary bodies, for its indisposition to enter directly into combination with the other elements, whence it follows that most of the compounds of carbon have to be obtained by indirect processes. This element appears, indeed, to be incapable of uniting with any other at the ordinary temperature, and this circumstance is occasionally turned to useful account, as when the ends of wooden stakes are charred before being plunged into the earth, when the action of the atmospheric oxygen, which, in the presence of moisture, would be very active in effecting the decay of the wood, is resisted by the charcoal into

which the external layer has been converted. The employment of black lead to protect metallic surfaces from rust is another application of the same principle. At a high temperature, however, carbon combines readily with oxygen, sulphur, and with some of the metals, and at a very high temperature, even with hydrogen. The tendency of carbon to combine with oxygen under the influence of heat, is shown when a piece of charcoal is strongly heated at one point, when the carbon at this point at once combines with the oxygen of the surrounding air (forming carbonic acid), and the heat developed by this combustion raises the neighbouring particles of carbon to the temperature at which the element unites with oxygen, and thus the combustion is gradually propagated throughout the mass, which is ultimately converted entirely into carbonic acid gas, nothing remaining but the white ash, composed of the mineral substances derived from the wood employed for preparing the charcoal. It is worthy of remark, that if charcoal had been a better conductor of heat, it would not have been so easily kindled, since the heat applied to any point of the mass would have been rapidly diffused over its whole bulk, and this point could not have attained the high temperature requisite for its ignition, until the whole mass had been heated nearly to the same degree; this is actually found to be the case in charcoal which has been very strongly heated (out of contact with air), when its conducting power is greatly improved, and it kindles with very great difficulty. The *calorific value* of carbon is represented by the number 8080, that is, 1 gr. of carbon, when burnt so as to form carbonic acid, is capable of raising 8080 grs. of water from 0° C. to 1° C.

A given weight of charcoal will produce twice as much available heat as an equal weight of wood, since the former contains more actual fuel and less oxygen, and much of the heat evolved by the wood is absorbed or rendered latent in the steam and other vapours which are produced by the action of heat upon it. (The attraction possessed by carbon for oxygen at a high temperature is turned to account in metallurgic operations, when coal and charcoal are employed for extracting the metals from their compounds with oxygen.*)

The unchangeable solidity of carbon is another remarkable feature. It is stated that some approach has been made, at extremely high temperatures, to the fusion and vaporisation of carbon, but it cannot be said to have been fairly established that this element is able to exist in any other than the solid form. Nor can any substance be found by the aid of which carbon may be brought into the liquid form by the process of solution, for although charcoal gradually disappears when boiled with sulphuric and nitric acids, it does not undergo a simple solution, but is converted, as will be seen hereafter, into carbonic acid.

54. COAL.—The various substances which are classed together under the name of coal are characterised by the presence of carbon as a largely predominant constituent, associated with smaller quantities of hydrogen, oxygen, nitrogen, sulphur, and certain mineral matters which compose the ash. Coal appears to have been formed by a peculiar decomposition or fermentation of buried vegetable matter, resulting in the separation of a large proportion of its hydrogen in the form of marsh-gas (CH_4), and

* Easily reducible oxides, such as oxide of lead, give carbonic acid when heated with charcoal; $2PbO + C = Pb_2 + CO_2$, but oxides which are not easily reducible, such as oxide of zinc, give carbonic oxide; $ZnO + C = CO + Zn$.

similar compounds, and of its oxygen in the form of carbonic acid (CO_2), the carbon accumulating in the residue. Thus, cellulose ($C_6H_{10}O_5$), which constitutes the bulk of woody fibre, might be imagined to decompose according to the equation $2C_6H_{10}O_5 = 5CH_4 + 5CO_2 + C_2$, and the occurrence of marsh-gas, and of the petroleum hydrocarbons of similar composition, as well as of carbonic acid, in connection with deposits of coal, supports this account of its formation. Marsh-gas and carbonic acid are the ordinary products of the fermentation of vegetable matter, and a spontaneous carbonisation is often witnessed in the "heating" of damp hay. But just as the action of heat upon wood produces a charcoal containing small quantities of the other organic elements, so the carbonising process by which the plants have been transformed into coal, has left behind some of the hydrogen, oxygen, and nitrogen; the last, as well probably as a little of the sulphur, having been derived from the vegetable albumen and similar substances which are always present in plants. The chief part of the sulphur is generally present in the form of iron pyrites, derived from some extraneous source. The examination of a peat-bog is very instructive with reference to the formation of coal, as affording examples of vegetable matter in every stage of decomposition, from that in which the organised structure is still clearly visible, to the black carbonaceous mass which only requires consolidation by pressure in order to resemble a true coal.

The three principal varieties of coal—*lignite, bituminous coal,* and *anthracite*—present us with the material in different stages of carbonisation; the lignite, or brown coal, presenting indications of organised structure, and containing considerable proportions of hydrogen and oxygen, while anthracite often contains little else than carbon and the mineral matter or ash. The following table shows the progressive diminution in the proportions of hydrogen and oxygen in the passage from wood to anthracite:—

	Carbon	Hydrogen.	Oxygen
Wood,	100	12·18	83·07
Peat,	100	9·85	55·67
Lignite,	100	8·37	42·42
Bituminous coal,	100	6·12	21·23
Anthracite,	100	2·84	1·74

The combustion of coal is a somewhat complex process, in consequence of the re-arrangement which its elements undergo when the coal is subjected to the action of heat.

As soon as a flame is applied to kindle the coal, the heated portion undergoes destructive distillation, evolving various combustible gases and vapours, which take fire and convey the heat to remoter portions of the coal. Whilst the elements of the exterior portion of coal are undergoing combustion, the heat thus evolved is submitting the interior of the mass to destructive distillation, resulting in the production of various compounds of carbon and hydrogen. Some of these products, such as marsh-gas (CH_4) and olefiant gas (C_2H_4), burn without smoke; while others, like benzole (C_6H_6) and naphthaline ($C_{10}H_8$), which contain a very large proportion of carbon, undergo partial combustion, and a considerable quantity of carbon, not meeting with enough heated oxygen in the vicinity to burn it entirely, escapes in a very finely divided state as smoke or soot, which is deposited in the chimney, mixed with a little carbonate of ammonia, and small quantities of other products of the distillation of coal. When the gas has been expelled from the coal, there remains a

mass of coke or cinder, which burns with a steady glow until the whole of its carbon is consumed, and leaves an *ash*, consisting of the mineral substances present in the coal. The final results of the perfect combustion of coal would be carbonic acid (CO_2), water (H_2O), nitrogen, a little sulphurous acid (SO_2), and ash. The production of smoke in a furnace supplied with coal may be prevented by charging the coal in small quantities at a time in front of the fire, so that the highly carbonaceous vapours must come in contact with a large volume of heated air before reaching the chimney. In arrangements for consuming the smoke, hot air is judiciously admitted at the back of the fire, in order to meet and consume the heated carbonaceous particles before they pass into the chimney.

The difference in the composition of the several varieties of coal gives rise to a great difference in their mode of burning.

The following table exhibits the composition of representative specimens of the four principal varieties :—

Composition of Coal.

	Lignite.	Bituminous Coal.	Wigan Cannel.	Anthracite.
Carbon,	66·32	78·57	80·06	90·39
Hydrogen,	5·63	5·29	5·53	3·28
Nitrogen,	0·56	1·84	2·12	0·83
Oxygen,	22·86	12·88	8·09	2·98
Sulphur,	2·36	0·39	1·50	0·91
Ash,*	2·27	1·03	2·70	1·61
	100·00	100·00	100·00	100·00

The lignites furnish a much larger quantity of gas under the action of heat, and therefore burn with more flame than the other varieties, leaving a coke which retains the form of the original coal; while bituminous coal softens and cakes together,—a useful property, since it allows even the dust of such coal to be burnt, if the fire be judiciously managed. Anthracite (*stone coal* or *Welsh coal*) is much less easily combustible than either of the others, and since it yields but little gas when heated, it usually burns with little flame or smoke. This variety of coal is so compact that it will not usually burn in ordinary grates, but is much employed for furnaces.

55. Carbon is capable of combining with oxygen in two proportions, forming the compounds known as *carbonic oxide* and *carbonic acid*, the composition of which is shown in the following table :—

Oxides of Carbon.

		Parts by weight. C	Parts by weight. O
Carbonic oxide,	CO,	12	16
Carbonic acid,	CO_2,	12	32

* The ash of coal consists chiefly of silica, alumina, and peroxide of iron.

CARBONIC ACID.

CO_2 44 parts by weight = 2 vols.

56. It has been already mentioned that carbonic acid is a component of the atmosphere, which usually contains about four volumes of carbonic acid in 10,000 volumes of air. This carbonic acid is chiefly formed by the operation of the atmospheric oxygen in supporting combustion and respiration.

All substances used as fuel contain a large proportion of carbon, which, in the act of combustion, combines with the oxygen, and escapes into the atmosphere in the form of carbonic acid.

In the process of respiration, the carbonic acid is formed from the carbon contained in the different portions of the animal frame to which oxygen is conveyed by the blood, having been taken up by the latter in passing through the lungs, where it gives out, in exchange for the oxygen, a quantity of carbonic acid produced by the union of a former supply of oxygen with the carbon of the different organs to which the blood is supplied, and which, as they are constantly corroded and destroyed by this oxidising action of the blood, are repaired by the supply of food taken into the body. This conversion of the carbon of the organs into carbonic acid will be again referred to; it will be at once evident that it must be concerned in the maintenance of the animal heat.

The leaves of plants, under the influence of light, have the power of decomposing the carbonic acid of the atmosphere, the carbon of which is applied to the production of vegetable compounds forming portions of the organism of the plant, and when this dies, the carbon is restored, after a lapse of time more or less considerable, to the atmosphere, in the same form, namely, that of carbonic acid, in which it originally existed there. If the plant should have been consumed as food by animals, its carbon will have been eventually converted into carbonic acid by respiration; the use of the plant as fuel, either soon after its death (wood), or after the lapse of time has converted it into coal, will also consign its carbon to the air in the form of carbonic acid. Even if the plant be left to *decay*, this process involves a slow conversion of its carbon into carbonic acid by the oxygen of the air.*

Putrefaction and *fermentation* are also very important processes concerned in restoring to the air, in the form of carbonic acid, the carbon contained in dead vegetable and animal matter. Although, in a popular sense, these two processes are distinct, yet their chemical operation is of the same kind, consisting in *the resolution of a complex substance into simpler forms, produced by contact with some other substance in a state of chemical change.* The discussion of the true nature of the process (which is even now somewhat obscure) would be premature at this stage, and it will suffice for the present to state that carbonic acid is one of the simpler forms into which the carbon is converted by the metamorphosis which ensues so quickly upon the death of animals and vegetables.

* In the dark, according to Boussingault, plants evolve carbonic acid. He found that a square metre (39·37 inches square) of oleander leaves decomposed, in sunlight, on an average, 1·108 litre (67·6 cubic inches) of carbonic acid every hour; whilst the same extent of leaf, in the dark, emitted 0·07 litre (4·27 cubic inches) of carbonic acid in the hour. Even under the influence of light, flowers have been found to absorb oxygen and evolve carbonic acid. —— like animals -

The production of carbonic acid in combustion, respiration, and fermentation, may be very easily proved by experiment. If a dry bottle be placed over a burning wax taper standing on the table, the sides of the bottle will be covered with dew from the combustion of the hydrogen in the wax; and if a little clear lime-water be shaken in the bottle, the milky deposit of carbonate of lime will indicate the formation of carbonic acid.

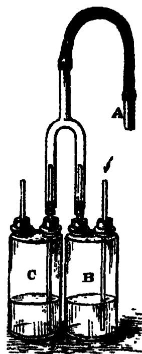


Fig. 64.

By arranging two bottles, as represented in fig. 64, and inspiring through the tube A, air will bubble through the lime-water in B, before entering the lungs, and will then be found to contain too little carbonic acid to produce a milkiness, but on expiring the air, it will bubble through C, and will render the lime-water in this bottle very distinctly turbid.

If a little sugar be dissolved in eight or ten times its weight of warm (not hot) water, in the flask A (fig. 65), and a little dried yeast, previously rubbed down with water, added, fermentation will commence in the course of an hour or less, and carbonic acid may be collected in the jar B.

57. In the mineral kingdom free carbonic acid is pretty abundant. The gas issues from the earth in some places in considerable quantity, as at Nauheim, where there is said to be a spring exhaling about 1,000,000 lbs. of the gas annually. Many spring waters, those of Seltzer and Pyrmont, for example, are very highly charged with the gas.

But it occurs in far larger quantity in a state of combination with lime, forming the immense deposits of *limestone*, marble, and chalk, which compose so large a portion of the crust of the globe. Carbonate of lime is also met with in the animal kingdom. Fish shells and pearls contain about two-thirds of their weight of this substance, whilst egg-shells contain as much as nine-tenths of carbonate of lime.

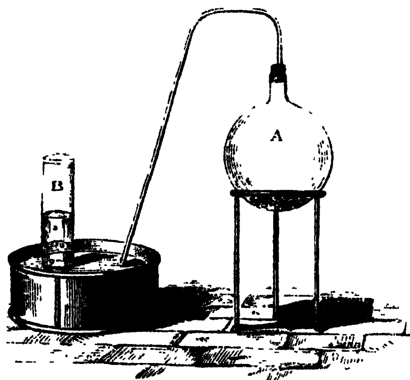
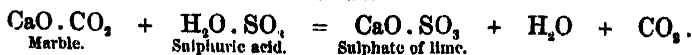


Fig. 65.

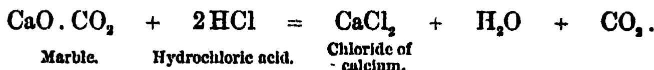
The expulsion of the carbonic acid from limestone ($CaO.CO_2$) forms the object of the process of *lime burning*, by which the large supply of lime (CaO) is obtained for building and other purposes. But if it be required to obtain the carbonic acid without regard to the lime, it is better to decompose the carbonate of lime with an acid.

Preparation of carbonic acid.—The form of the carbonate of lime, and the nature of the acid employed, are by no means matters of indifference. If dilute sulphuric acid be poured upon fragments of marble, the effervescence which occurs at first soon ceases, for the surface of the marble becomes coated with the nearly insoluble sulphate of lime, by which it is protected from the further action of the acid—



$$\underset{\text{Marble.}}{CaO.CO_2} + \underset{\text{Sulphuric acid.}}{H_2O.SO_4} = \underset{\text{Sulphate of lime.}}{CaO.SO_3} + H_2O + CO_2.$$

if the marble be finely powdered, or if powdered chalk be employed, each particle of the carbonate of lime will be acted upon. When lumps of carbonate of lime are acted upon by hydrochloric acid, there is no danger that any will escape the action of the acid, for the chloride of calcium produced is one of the most soluble salts—



$$CaO.CO_2 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Marble. Hydrochloric acid. Chloride of calcium.

For the ordinary purposes of experiment, carbonic acid is most easily obtained by the action of diluted hydrochloric acid upon small fragments of marble (fig. 66), the latter being covered with water, and hydrochloric acid poured in through the funnel-tube. The gas may be collected by downward displacement.

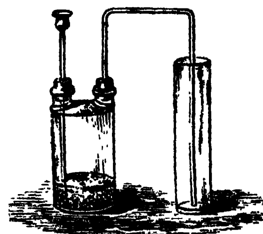


Fig. 66. - Preparation of carbonic acid.

58. *Properties of carbonic acid.*—Carbonic acid gas is invisible, like the gases already examined, but is distinguished by a peculiar pungent odour, as is perceived in soda-water. It is more than half as heavy again as atmospheric air, its specific gravity being 1·529, which causes its accumulation near the floor of such confined spaces as the Grotto del Cane, where it issues from fissures in the rock.

The high specific gravity of carbonic acid may be shown by pouring it into a light jar attached to a balance, and counterpoised by a weight in the opposite scale (fig. 67).



Fig. 67.

Another favourite illustration consists in floating a soap-bubble on the surface of a layer of the gas generated in the large jar (fig. 68), by pouring diluted sulphuric acid upon a few ounces of chalk made into a thin cream with water.

If a small balloon, made of collodion, be placed in the jar A (fig. 69), it will ascend on the admission of carbonic acid through the tube B.

If smouldering brown paper be held at the mouth of a jar, like that in fig. 69, the smoke will float upon the surface of the carbonic acid, and will sink with it on removing the stopper.

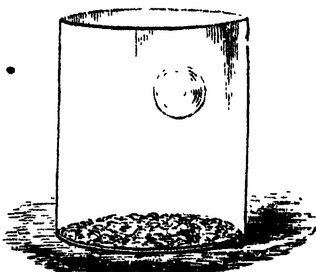


Fig. 68.

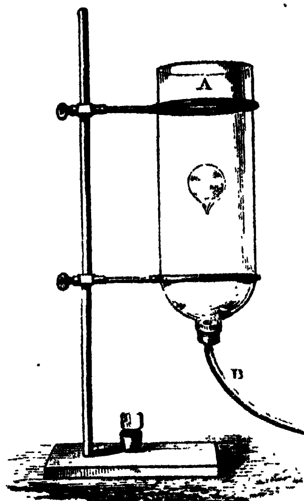


Fig. 69.

The power which carbonic acid possesses of extinguishing flame is very important, and has received practical application in the case of burning mines which must otherwise have been flooded with water.* Many attempts have also been made from time to time to employ this gas for subduing ordinary conflagrations, but their success has hitherto been very partial. It will be remembered that pure nitrogen is also capable of extinguishing the flame of a taper, but a large proportion of this gas may be present in air without affecting the flame, whereas a taper is extinguished in air containing one-eighth of its volume of carbonic acid, and is sensibly diminished in brilliancy by a much smaller proportion of the gas.

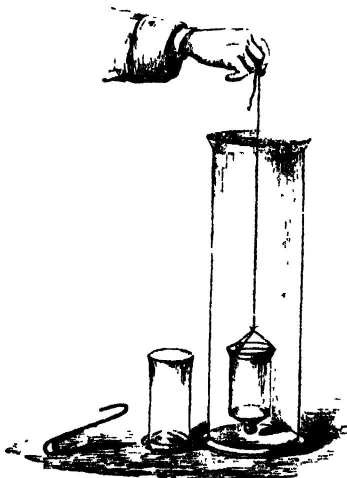


Fig. 70.

The power of extinguishing flame, conjoined with the high density of carbonic acid, admit of some very interesting illustrations.

Carbonic acid may be poured from some distance upon a candle, and will extinguish it at once.

A large torch of blazing tow may be plunged beneath the surface of the carbonic acid in the jar, fig. 68.

Carbonic acid may be raised in a glass bucket (fig. 70) from a large jar, and poured into another jar the air in which has been previously tested with a taper.

A wire stand with several tapers fixed at different levels may be placed in the jar A, fig. 71, and carbonic acid gradually admitted through a flexible tube connected

* All gases which take no part in combustion may extinguish flame, even in the presence of air, by absorbing heat and reducing the temperature below the burning-point.

with the neck of the jar, from the cistern B, a hole in the cover of which allows air to enter it as the gas flows out; the flame of each taper will gradually expire as the surface of the carbonic acid rises in the jar.

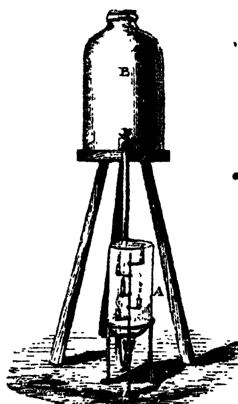


Fig. 71.

A jar of oxygen may be placed over a jar of carbonic acid, as shown in fig. 53, and a taper let down through the oxygen, in which it will burn brilliantly, into the carbonic acid, which extinguishes it, and if it be quickly raised again into the oxygen, it will rekindle with a slight detonation. This alternate extinction and rekindling may be repeated several times.

On account of this extinguishing power of carbonic acid, a taper cannot continue to burn in a confined portion of air until it has exhausted the oxygen, but only until its combustion has produced a sufficient quantity of carbonic acid to extinguish the flame.

To demonstrate this, advantage may be taken of the circumstance that phosphorus will continue to burn in spite of the presence of carbonic acid. Upon the stand A (fig. 72) a small piece of phosphorus is placed, and a taper is attached to the stand by a wire. The cork B fits air-tight into the jar, and carries a piece of copper wire bent so that it may be heated by the flame of the taper. A little water is poured into the plate to prevent the entrance of any fresh air. If the taper be kindled, and the jar placed over it, the flame will soon die out; and on moving the jar so that the hot wire may touch the phosphorus, its combustion will show that a considerable amount of oxygen still remains.



Fig. 72.

In the same manner, an animal can breathe a confined portion of air only until he has charged it with so much carbonic acid that the hurtful effect of this gas begins to be felt, a considerable quantity of oxygen still remaining.

If the air contained in the jar A (fig. 73), standing over water, be breathed two or three times through the tube B, a painful sense of oppression will soon be felt in consequence of the accumulation of carbonic acid. By immersing a deflagrating spoon C, containing a piece of burning phosphorus, and having a lighted taper attached, it may be shown that although there is enough carbonic acid to extinguish the taper, the oxygen is not exhausted, for the phosphorus continues to burn rapidly.

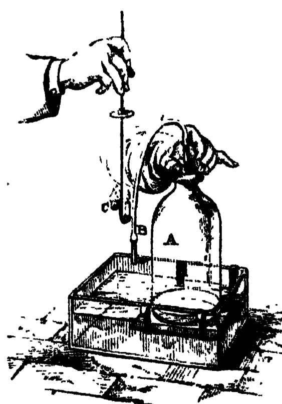


Fig. 73.

Carbonic acid is not poisonous when taken into the stomach, but acts most injuriously when breathed, by offering an obstacle to that escape of carbonic acid, by diffusion, from the blood of the venous circulation in the lungs, and its consequent replacement by the oxygen necessary to arterial blood. Any hindrance to this interchange must impede respiration, and such hindrance would, of course, be afforded by carbonic acid present in the air inhaled, in proportion to its quantity. The difference in constitution and

temperament in individuals makes it impossible that any exact general rule should be laid down as to the precise quantity of carbonic acid which may be present in air without injury to respiration, but it may be safely asserted that it is not advisable to breathe for any length of time in air containing more than $\frac{1}{1000}$th (0·1 per cent.) of its volume of carbonic acid.

There appears to be no immediate danger, however, until the carbonic acid amounts to $\frac{1}{200}$th (0·5 per cent.), when most persons are attacked by the languor and headache attending the action of this gas. A larger proportion of carbonic acid produces insensibility, and air containing $\frac{1}{12}$th of its volume of carbonic acid causes suffocation. The danger in entering old wells, cellars, and other confined places, is due to the accumulation of this gas, either exhaled from the earth or produced by decay of organic matter. The ordinary test applied to such confined air by introducing a candle is only to be depended upon if the candle burns as brightly in the confined space as in the external air; should the flame become at all dim, it would be unsafe to enter, for experience has shown that combustion may continue for some time in an atmosphere dangerously charged with carbonic acid.

The accidents from *choke damp* and *after damp* in coal mines, and from the accumulation, in brewers' and distillers' vats, of the carbonic acid resulting from fermentation, are also examples of the fatal effect of this gas.

The air issuing from the lungs of a man at each expiration contains from 3·5 to 4 volumes of carbonic acid in 100 volumes of air, and could not, therefore, be breathed again without danger. The total amount of carbonic acid evolved by the lungs and skin amounts to about 0·7 cubic foot per hour. In order that it may be breathed again without inconvenience, this should be distributed through at least 140 cubic feet of fresh air, or a space measuring 5·2 feet each way. Hence the necessity for a constant supply of fresh air by ventilation, to dilute the carbonic acid to such an extent that it may cease to impede respiration. This becomes the more necessary where an additional quantity of carbonic acid is supplied by candles or gas-lights. Two ordinary gas-burners, each consuming three cubic feet of gas per hour, will produce as much carbonic acid as one man. Fortunately, a natural provision for ventilation exists in the circumstance that the processes of respiration and combustion, which contaminate the air, also raise its temperature, thus diminishing its specific gravity by expansion, and causing it to ascend and give place to fresh air. Hence the vitiated air always accumulates near the ceiling of an apartment, and it becomes necessary to afford it an outlet by opening the upper sash of the window, since the chimney ventilates immediately only the lower part of the room.

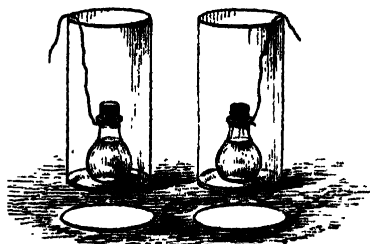


Fig. 74.

These principles may be illustrated by some very simple experiments.

Two quart jars (fig. 74) are filled with carbonic acid, and after being tested with a taper, a 4 oz. flask is lowered into each, one flask containing cold and the other hot water. After a few minutes, the jar with the cold flask will still contain enough

carbonic acid to extinguish the taper, whilst the air in the other jar will support combustion brilliantly.

A tall stoppered glass jar (fig. 75) is placed over a stand, upon which three lighted tapers are fixed at different heights. The vitiated air, rising to the top of the jar, will extinguish the uppermost taper first, and the others in succession. By quickly removing the stopper and raising the jar a little before the lowest taper has expired, the jar will be ventilated and the taper revived.

A similar jar (fig. 76), with a glass chimney fixed into the neck through a cork or piece of vulcanised tubing, is placed over a stand with two tapers, one of which is near the top of the jar, and the other beneath the aperture of the chimney; if a crevice for the entrance of air be left between the jar and the table, the lower taper will continue to burn indefinitely, whilst the upper one will soon be extinguished by the carbonic acid accumulating around it.

In ordinary apartments, the incidental crevices of the doors and windows are depended upon for the entrance of fresh air, whilst the contaminated air passes out by the chimney, but in large buildings special provision must be made for the two air currents. In mines this becomes the more necessary, since the air receives much additional contamination by the

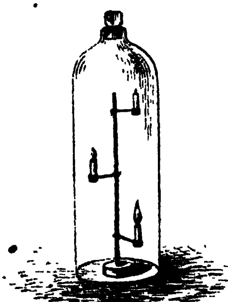


Fig. 75.

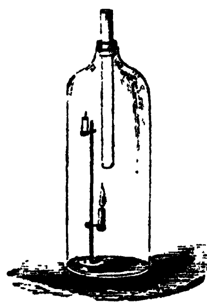


Fig. 76.

gases (marsh-gas and carbonic acid) evolved from the workings, and by the smoke occasioned in blasting with gunpowder. Mines are generally provided with two shafts for ventilation, under one of which (the *upcast* shaft) a fire is maintained to produce the upward current, which carries off the foul air, whilst the fresh air descends by the other (*downcast* shaft). The current of fresh air is forced by wooden partitions to divide itself, and pass through every portion of the workings.

The operation of such provisions for ventilation is easily exhibited.

A tall jar (fig. 77) is fitted with a ring of cork, carrying a wide glass chimney (A). If this be placed over a taper standing in a plate of water, the accumulation of vitiated air will soon extinguish the taper; but if a second chimney (B), supported in a wire ring, be placed within the wide chimney, fresh air will enter through the interval between the two, and the smoke from a piece of brown paper will demonstrate the existence of the two currents, as shown by the arrows.

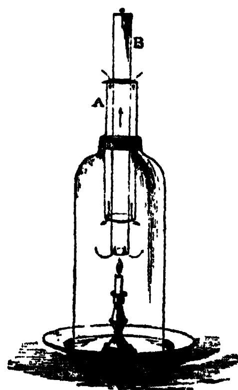


Fig. 77.

A small box (fig. 78) is provided with a glass chimney at each end. In one of these (B) representing the upcast shaft, a lighted taper is suspended. A piece of smoking brown paper may be held in each chimney to show the direction of the current. On closing A with a glass plate, the taper in B will be extinguished, the entrance of fresh air being prevented. By breathing gently into A the taper will also be

extinguished. The experiment may be varied by pouring carbonic acid and oxygen alternately into A, when the taper will be extinguished and rekindled by turns.

A pint bell-jar (fig. 79) is placed over a taper standing in a tray of water. If a chimney (a common lamp-glass) be placed on the top of the jar, the flame of the taper will gradually die out, because no provision exists for the establishment of the two currents, but on dropping a piece of tin-plate or card-board into the chimney, so as to divide it, the taper will be revived, and the smoke from the brown paper will distinguish the upcast from the downcast shaft.

If a little water be poured into a wide-mouthed bottle of carbonic acid, and the bottle be then firmly closed by the palm of the hand, it will be found, on shaking the bottle violently, that the carbonic acid is absorbed, and the palm of the hand is sucked into the bottle. The presence of carbonic acid in the solution may be proved by pouring it into lime-water, in which it will produce a precipitate of carbonate of lime, redissolved by a further addition of the solution of carbonic acid.

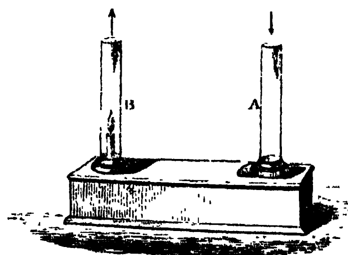
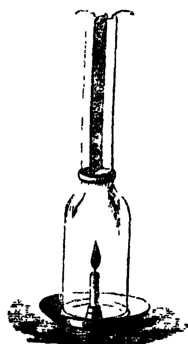


Fig. 78.

One pint of water shaken in a vessel containing carbonic acid gas, at the ordinary pressure of the atmosphere, will dissolve about one pint of the gas, equal in weight to nearly 16 grains. If the carbonic acid be confined in the vessel under a pressure equal to twice or thrice that of the atmosphere—that is, if twice or thrice the quantity of carbonic acid be compressed into the same space, the water will still dissolve one pint of the gas, but the weight of this pint will now be twice or thrice that of the pint of uncompressed gas, so that the water will have dissolved 32 or 48 grains of the gas, accordingly as the pressure had been doubled or trebled. As soon, however, as the pressure is removed, the compressed carbonic acid will resume its former state, with the exception of that portion which the water is capable of retaining in solution under the ordinary pressure of the atmosphere. Thus, if the water had been charged with carbonic acid under a pressure equal to thrice that of the atmosphere, and had therefore absorbed 48 grains of the gas, it would only retain 16 grains when the pressure was taken off, allowing 32 grains to escape in minute bubbles, producing the appearance known as *effervescence*. This affords an explanation of the properties of soda-water, which is prepared by charging water with carbonic acid gas under considerable pressure, and rapidly confining it in strong bottles. As soon as the resistance offered by the cork to the expansion of the gas is removed, the excess of the carbonic acid, above that which it can hold in solution at the ordinary pressure of the air, escapes with effervescence. In a similar manner, the waters of certain springs become charged with carbonic acid, under high pressure, beneath the surface of the earth, and when, upon their rising to the surface, this pressure is removed, the excess of carbonic acid escapes with effervescence, giving rise to the sparkling appearance and sharp flavour which renders spring water so agreeable. On the other hand, the waters of lakes and


Fig. 79.

rivers are usually flat and insipid, because they hold in solution so small a quantity of uncombined carbonic acid.

The sparkling character of champagne, bottled beer, &c., is due to the presence in these liquids of a quantity of carbonic acid which has been generated by fermentation, subsequent to bottling, and has therefore been retained in the liquid under pressure. In the case of Seidlitz powders and soda-water powders, the effervescence caused by dissolving them in water is due to the disengagement of carbonic acid, caused by the action of the tartaric acid, which composes one of the powders, upon the bicarbonate of soda, producing tartrate of soda and carbonic acid gas. In the dry state these powders may be mixed without any chemical change, but the addition of water immediately causes the effervescence.

The solubility of carbonic acid in water is of great importance in the chemistry of Nature; for this acid, brought down from the atmosphere dissolved in rain, is able to act chemically upon rocks, such as granite, which contain alkalies—the carbonic acid combining with these, and thus slowly disintegrating or crumbling down the rock, an effect much assisted by the mechanical action of the expansion of freezing water in the interstices of the rock. It appears that soils are thus formed by the slow degradation of rocks, and when these soils are capable of supporting plants, the solution of carbonic acid is again of service, not only as a direct food, by providing the plant with carbon through its roots, but as a solvent for certain portions of the mineral food of the plant (such as phosphate of lime), which pure water could not dissolve, and which the plant cannot take up except in the dissolved state.

59. Although carbonic acid retains its state of gas under all temperatures and pressures to which it is commonly exposed, it is capable of assuming the liquid and even the solid state.

At about the ordinary temperature (59° F.) carbonic acid is condensed, by a pressure of 50 atmospheres (750 lbs. per square inch), to a colourless liquid of sp. gr. 0·83 (water = 1), and at a temperature of—70° F. (70° below the zero, or 102° below the freezing point, F.) becomes a transparent mass of solid carbonic acid resembling ice.

If the temperature of the gas be reduced to 32° F. a pressure of 38·5 atmospheres only will suffice to liquefy it.

The experiments of Andrews upon the liquefaction of carbonic acid show that, in causing the liquefaction of gases, increase of pressure is not always equivalent to reduction of temperature, but that there exists a particular temperature for each gas above which no amount of pressure is able to liquefy it, and at this particular temperature, the *critical point*, the gas is wavering between the gaseous and the liquid state, so that "the gaseous and liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle, that the passage shall nowhere present any interruption or breach of continuity." It was found to be impossible to liquefy carbonic acid above a temperature of 88° F., even by a pressure of 109 atmospheres; but, at this high pressure, the gas ceased to obey the law that the volume of a gas is inversely as the pressure, for instead of occupying $\frac{1}{109}$ of its original volume, it had been reduced to $\frac{1}{430}$. On cooling the gas thus compressed, it liquefied suddenly, and not gradually as in the case of a vapour under ordinary pressure. The gas in this condition, when subjected to very small variations of temperature or pressure, exhibits curious flickering movements, resembling the effect produced by the ascent of columns of heated air through colder strata.

Even at 55° F., a pressure of 48·89 atmospheres reduced the gas (not to $\frac{1}{49}$ but) to $\frac{1}{51}$ of its original volume without liquefying it, but at this point, an additional pressure of only $\frac{1}{50}$ atmosphere suddenly liquefied one half of the gas.

A small specimen of liquid carbonic acid is easily prepared. A strong tube of green glass (A, fig. 80 is selected, about 12 inches long, $\frac{5}{8}$ inch diameter in the bore, and $\frac{1}{10}$ inch thick in the walls. With the aid of the blowpipe flame this tube is softened and drawn off at about an inch from one end, as at B, which is thus closed (C). This operation should be performed slowly, in order that the closed end may not be much thinner than the walls of the tube. When the tube has cooled, between 30 and 40 grs. of powdered bicarbonate of ammonia (ordinary sesquicarbonate which has crumbled down) are tightly rammed into it with a glass rod. This part of the tube is then surrounded with a few folds of wet blotting-paper to keep it cool, and the tube is bent, just beyond the carbonate of ammonia, to a somewhat obtuse angle (D). The tube is then softened at about an inch from the open end, and drawn out to a narrow neck (E), through which a measured drachm of oil of vitriol is poured down a funnel-tube, so as not to soil the neck, which is then carefully drawn out and sealed by the blowpipe flame, as at F. The empty space in the tube should not exceed $\frac{1}{4}$ cubic inch.

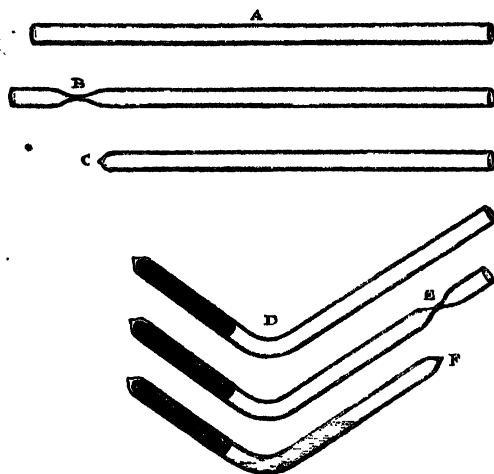


Fig. 80.

When the tube is thoroughly cold, it is suspended by strings in such a position that the operator, having retired behind a screen at some distance, may reverse the tube, allowing the acid to flow into the limb containing the carbonate of ammonia; or the tube may be fixed in a box which is shut up, and reversed so as to bring the tube into the required position.

If the tube be strong enough to resist the pressure, it will be found, after a few hours, that a layer of liquid carbonic acid has been formed upon the surface of the solution of sulphate of ammonia. By cooling the empty limb in a mixture of pounded ice and salt, or of hydrochloric acid and sulphate of soda, the liquid acid can be made to distil itself over into this limb, leaving the sulphate of ammonia in the other.

Fig. 81 represents Thilorier's apparatus for the preparation of several pints of liquid carbonic acid. *g* is a strong *wrought iron generator* of gas in which 2 lbs. of bicarbonate of soda are well stirred with 4 pints of water at 100° F. Half a pint of oil of vitriol is poured into a brass tube which is dropped upright into the generator, as shown by the dotted lines in the figure, which also indicate the level of the liquid in the generator. The head of the generator is then firmly screwed on, with the help of the spanners represented in the figure, and the stopcock* firmly closed by turning the wheel *w*. The generator is then turned over and over on its trunnions resting upon the stand *s*, for ten minutes, so that the whole of the sulphuric acid may be mixed with the solution of bicarbonate of soda. The generator is then connected, by the copper tube *t* with the strong wrought iron *receiver r*, the stopcock of which is attached to a tube passing down to the bottom of the vessel. The stopcock of the receiver is then opened, by turning the wheel *v*, and afterwards that of the generator.

The condensed gas then passes over into the receiver. After two or three minutes the stopcocks are again closed, the generator detached, the waste gas blown out through the stopcock, the head unscrewed, and the generator emptied and recharged. After the operation has been repeated three times, the pressure in the receiver will be found to have liquefied some of the carbonic acid, and after seven charges, the receiver is nearly filled with the liquid acid. The tube *t* is then unscrewed from the

* These stopcocks are steel screws with conical points fitting into gun-metal sockets. Leaden washers are employed to secure the tightness of the joints between the iron vessels and their heads, which are made of gun-metal.

receiver, and replaced by the nozzle *n*. If the stopcock be then slightly opened, a stream of the liquid will be forced up the tube, and, issuing into the air, will congeal by its own evaporation into an opaque white spray of solid carbonic acid.

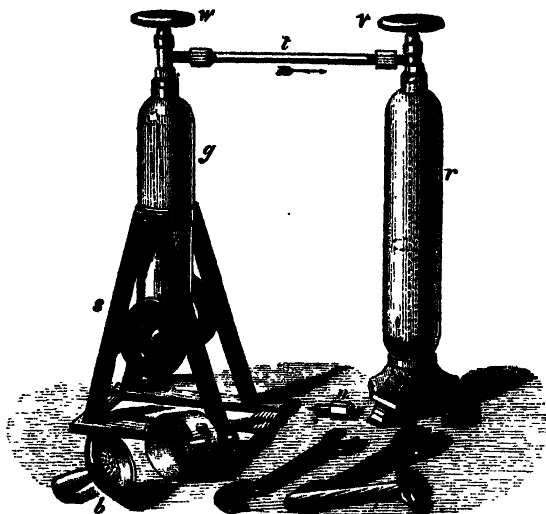


Fig. 81.—Liquefaction of carbonic acid.

In order to collect the solid, the box shown at *b* is employed. This is made of brass, and furnished with strong flanges by which the cover is secured to it. The handles of the box are made of wood or gutta percha, and are hollow, with brass tubes passing through them to allow of the escape of the gaseous carbonic acid, the ends of the tubes within the box being covered by perforated plates which prevent the escape of the solid acid. The box and its cover having been fitted together, the nozzle of the receiver *r* is inserted into a short tube projecting from the side of the box, and whilst one operator holds the box firmly by the handles, another gradually opens the stopcock by turning the wheel *v*. A stream of the liquid acid is at once forced into the box, where it strikes against a curved brass plate arranged so as to force it to pass all round the inside of the box; about seven-eighths of it evaporate as gas, which rushes out through the tubular handles, and the rest is found in the box in a solid state, resembling snow. It should be quickly shaken on to a sheet of paper, and emptied into a beaker placed within a larger beaker, the interval being filled up by flannel. By covering the beaker with a dial glass, the solid acid may be kept for some time. The box becomes intensely cold, and condenses the moisture of the air to a thick layer of hoar frost, and if it be dipped into water it becomes coated with ice.



Fig. 82.

The solid carbonic acid evaporates without melting, for its melting-point is − 85° F., and its own evaporation keeps it at − 125° F. It produces a sharp sensation of cold when placed upon the hand, and if pressed into actual contact with the skin, causes a painful frost-bite. Its rapid evaporation may be shown by placing a few fragments on the surface of water in the globe (fig. 82), which has a tube passing down to the bottom, through which the pressure of the carbonic gas forces the water to a considerable height.

The solid carbonic acid is soluble in ether, and it evaporates from this solution far more rapidly, because the liquid is a better conductor of heat than the highly porous solid, and abstracts heat more rapidly from surrounding objects.

If a layer of ether be poured upon water, and some solid carbonic acid be thrown into it, the water is covered with a layer of ice.

On immersing the bulb of a thermometer into the solution of solid carbonic acid in ether, the mercury becomes solid, and the bulb may be hammered out into a disk.

By placing a piece of filter-paper in an evaporating dish, pouring a pound or so of mercury into it, immersing a wire turned into a flat spiral at the end, covering the mercury with ether,* and throwing in some solid carbonic acid, the mercury may soon be frozen into a cake. If this be suspended by the wire in a vessel of water, the mercury melts, descending in silvery streams to the bottom of the vessel, leaving a cake of ice on the wire, with icicles formed during the descent of the mercury.

Even in a red hot vessel, with prompt manipulation, the mercury may be solidified by the solution of solid carbonic acid in ether.

The temperature produced by the evaporation of the solid carbonic dissolved in ether is estimated at $-150°$ F.

60. Carbonic acid may be separated from most other gases by the action of hydrate of potash, which absorbs it, forming carbonate of potash. The proportion of carbonic acid is inferred either from the diminution in volume suffered by the gas when treated with potash, or from the increase of weight of the latter.

In the former case the gas is carefully measured over mercury (fig. 83), with due attention to temperature and barometric pressure, and a little concentrated solution of potash is thrown up through a curved *pipette* or syringe, introduced into the orifice of the tube beneath the surface of the mercury. The tube is gently shaken for a few seconds to promote the absorption of the gas, and, after a few minutes' rest, the diminution of volume is read off. Instead of solution of potash, damp hydrate of potash in the solid state is sometimes introduced, in the form of small sticks or balls attached to a wire. To determine the weight of carbonic acid in a gaseous mixture, the latter is passed through a bulb-apparatus (C, fig. 84), containing a strong solution of potash, and weighed before and after the passage of the gas. When the proportion of carbonic acid in the gas is small, it is usual to attach to the bulb-apparatus a little tube, containing solid hydrate of potash, or chloride of calcium, or pumice stone moistened with sulphuric acid, for the purpose of retaining any vapour of water which the large volume of unabsorbed gas might carry away in passing through the solution of potash.

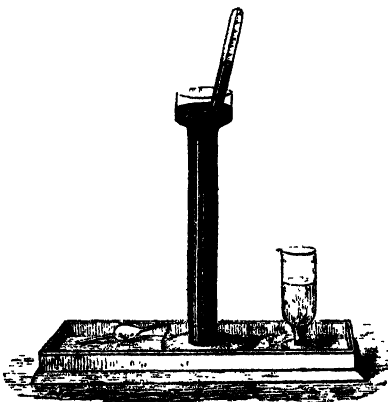


Fig. 83.

61. *Ultimate organic analysis.*—It is necessary to determine in this manner the weight of carbonic acid, in order to ascertain the proportion of carbon present in organic substances. For this purpose, an accurately weighed quantity (usually from seven to ten grains) of the organic substance is very carefully mixed with some compound from which it can obtain oxygen at a high temperature, such as oxide of copper (CuO) or chromate of lead ($PbO.CrO_3$), care being taken to employ a large excess of the oxidising agent. The mixture is introduced into a *combustion-tube* of German glass (which is free from lead and noted for its infusibility) of the form shown in A, fig. 84. This tube is provided with a small tube B, containing chloride of calcium, which is connected by a tube of caoutchouc with the potash-bulbs C. On gradually heating the tube in a charcoal

* Much economy of solid carbonic acid results from the use of the *anæsthetic* ether in these experiments.

furnace, or over a properly constructed gas-burner, the hydrogen and carbon contained in the organic substance are converted, respectively, into water and carbonic acid, by the oxygen derived from the chromate of lead or oxide of copper. The water is absorbed by the chloride of calcium in B, and the increase of weight in this tube will indicate the quantity of water formed in the combustion, whilst that of the potash bulbs will show the weight of the carbonic acid. When the whole length of the tube is red hot, and no more gas passes through the bulbs, the sealed point D of the tube is broken off, and air drawn through by applying suction at E, in

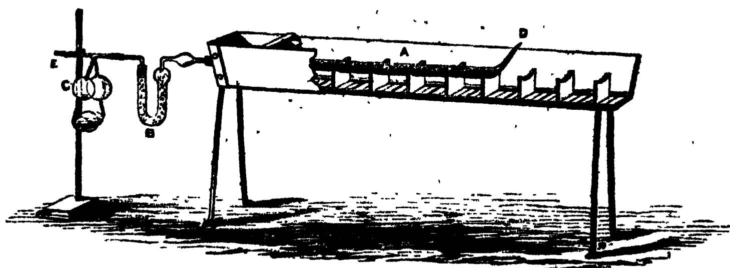


Fig. 84.—Apparatus for organic analysis.

order to sweep out the last traces of water and carbonic acid into the chloride of calcium and potash. Sometimes the organic substance is heated in a little platinum tray, placed within a glass tube, through which a stream of pure oxygen is passed, the products of combustion being afterwards made to pass over red hot oxide of copper, to convert any carbonic oxide into carbonic acid, and collected for weighing as before.

When the organic substance contains carbon, hydrogen, and oxygen, the weight of this last is inferred by subtracting the weights of the carbon and hydrogen from that of the substance. As an example of the *ultimate analysis of an organic substance*, the results of an analysis of oxalic acid are here given—

10 grs. of oxalic acid, dried at 212° F., gave 9·78 grs. of carbonic acid and 2·00 grs. of water.

$$\underset{44}{CO_2} : \underset{12}{C} :: \underset{9\cdot78}{CO_2} : x$$

$x = 2\cdot67$ grs. of carbon in 10 grs. of oxalic acid.

$$\underset{18}{H_2O} : \underset{2}{H_2} :: \underset{2\cdot00}{H_2O} : y$$

$y = 0\cdot22$ gr. of hydrogen in 10 grs. of oxalic acid.

It having been ascertained by preliminary experiments that oxalic acid contains only carbon, hydrogen, and oxygen, 10 (oxalic acid) *minus* 2·89 (carbon and hydrogen) = 7·11 grs. of oxygen in 10 grs. of oxalic acid.

It appears, therefore, that

10 grs. of oxalic acid contain
2·67 „ carbon,
0·22 „ hydrogen, and
7·11 „ oxygen.

Empirical and rational formulæ.—In order to deduce from these numbers the chemical formula for oxalic acid, that is, the formula expressing the number of atoms of each element, it will be necessary, of course, to divide the weight of each element by the number representing its atomic weight.

Thus 2·67 ÷ 12 = 0·22 atomic proportion of carbon;
0·22 ÷ 1 = 0·22 ,, ,, hydrogen;
7·11 ÷ 16 = 0·44 ,, ,, oxygen.

And the formula of oxalic acid might be written $C_{.22}H_{.22}O_{.44}$. But as fractions are not admissible in such a formula, it would be written $C_{22}H_{22}O_{44}$. This, however, is only an *empirical* formula for oxalic acid, that is, a formula which represents its *composition* only, without reference to its *constitution*, *i.e.*, to the absolute number of atoms present, and to the mode in which they are grouped or arranged within the compound. A formula professing to give such information would be termed a *rational* formula, and can only be arrived at by the careful study of the relation of the substance under examination to others of which the combining weights are certainly known. Thus, it is found that one molecule (56 parts) of caustic potash (KHO) requires 45 parts of dry oxalic acid to neutralise it and form the oxalate of potash. Hence it is reasonable to regard 45 as the molecular weight of dry oxalic acid. Since the above analysis has proved this quantity of oxalic acid to contain 12 (one atom) of carbon, 1 (one atom) of hydrogen, and 32 (two atoms) of oxygen, the formula would be written CHO_2. The action of oxalic acid upon caustic potash would then be represented by the equation $KHO + CHO_2 = H_2O + CKO_2$ (oxalate of potash). But there is another oxalate which has the formula C_2KHO_4 (binoxalate of potash) in which only one half of the hydrogen is displaced by potassium. Hence there must be two atoms of hydrogen in the molecule of oxalic acid, and its formula is $C_2H_2O_4$. In determining whether this formula represents only one grouping of the elements, or whether it contains two or more groups in combination, the chemist is guided by the results of a more minute study of the decompositions which the compound undergoes under varied conditions.

62. *Salts formed by carbonic acid.*—Although so ready to combine with the alkalies and alkaline earths (as shown in its absorption by solution of potash and by lime-water), carbonic acid must be classed among the weaker acids. It does not neutralise the alkalies completely, and it may be displaced from its combinations with bases by most other acids. Its action upon the colouring matter of litmus is feeble and transient. If a solution of carbonic acid in water be added to blue infusion of litmus, a wine-red liquid is produced, which becomes blue again when boiled, losing its carbonic acid; whilst litmus reddened by sulphuric, hydrochloric, or nitric acid, acquires a brighter red colour, which is permanent on boiling.

With each of the alkalies carbonic acid forms two well-defined salts, the *carbonate* and *bicarbonate*. Thus, the carbonates of potash and soda are represented by the formulæ, $K_2O.CO_2$ and $Na_2O.CO_2$, whilst the bicarbonates are $KHO.CO_2$ and $NaHO.CO_2$. The existence of the latter salts would favour the belief in the existence of a hydrate of carbonic acid ($H_2O.CO_2$), although no such combination of water with carbonic acid has yet been obtained in the separate state. Perfectly dry carbonic acid

gas is not absorbed by pure quicklime (CaO), but when a little water is added, combination at once takes place. This supports the view entertained, by some chemists, that CO_2 is not an acid until it is associated with water, and they therefore speak of it as *carbonic anhydride,* reserving the name carbonic acid for the as yet undiscovered compound $H_2O.CO_2$ (or H_2CO_3).

Opposed to this view, however, is the fact that quicklime will absorb carbonic acid when heated to a certain point.

Two hard glass tubes closed at one end, and bent as in fig. 85, are perfectly dried, and filled, over mercury, with well-dried carbonic acid gas. Fragments of lime are taken, whilst red hot, out of a crucible, cooled under the mercury, inserted into the tubes, and transferred to the upper end. No absorption of the carbonic acid takes place, though the tubes be left for some days; but if one of them be heated by a Bunsen burner, the absorption of carbonic acid takes place rapidly, and the mercury is forced up into the tube.

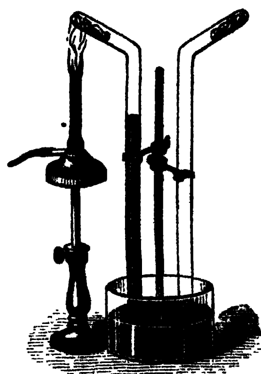


Fig. 85.

The carbonates may be expressed either by *additive* formulæ, showing the bases which combine with carbonic acid to produce them, or by *substitutive* formulæ, in which they are represented as formed from the *hypothetical* H_2CO_3 by the substitution of metals for the hydrogen. In the latter formulæ the existence of CO_2 is lost sight of altogether.

The following are some of the principal carbonates which are found in nature or employed in the arts :—

Chemical Name.	Common Name.	Additive Formula.	Substitutive Formula.
Carbonate of potash	Potashes, Pearl-ash	$K_2O\ .\ CO_2$	K_2CO_3
Bicarbonate of potash		$K_2O\ .\ H_2O\ .\ 2CO_2$	$KHCO_3$
Carbonate of soda	Alkali Washing soda	$Na_2O\ .\ CO_2$	Na_2CO_3
Bicarbonate of soda	Carbonate of soda	$Na_2O\ .\ H_2O\ .\ 2CO_2$	$NaHCO_3$
Sesquicarbonate of ammonia	Smelling salts Preston salts Carbonate of ammonia	$4NH_3.2H_2O.3CO_2$	$2[(H_4N)_2CO_3]CO_2$
Carbonate of lime	Limestone, chalk Marble	$CaO\ .\ CO_2$	$CaCO_3$
Basic carbonate of magnesia	*Magnesia alba* Magnesia	$3(MgO\ .\ CO_2)$, $MgO\ .\ H_2O.$	$3MgCO_3\ .\ MgH_2O_2$
Carbonate of iron	Spathic iron ore	$FeO\ .\ CO_2$	$FeCO_3$
Carbonate of zinc	Calamine	$ZnO\ .\ CO_2$	$ZnCO_3$
Basic carbonate of copper	Malachite	$CuO\ .\ CO_2$, $CuO\ .\ H_2O$	$CuO\ .\ H_2O\ .\ CuCO_3$
Basic carbonate of lead	White lead	$2(PbO\ .\ CO_2)$, $PbO\ .\ H_2O$	$2PbCO_3\ .\ PbO\ .\ H_2O$
Double carbonate of lime and magnesia	Dolomite Magnesian limestone	$CaO\ .\ MgO\ .\ 2CO_2$	$MgCa2CO_3$

63. *Analytical proof of the composition of carbonic acid.*—Lavoisier appears to have been the first to prove that carbonic acid was formed when carbon combined with oxygen, but its composition was first analytically demonstrated by Smithson Tennant, who heated carbonate of lime with phosphorus in a sealed glass tube, and obtained phosphate of lime and carbon, the latter having parted with its oxygen to convert the phosphorus into phosphoric acid.

A far easier method of demonstrating the composition of carbonic acid consists in introducing a pellet of potassium into a bulb tube, through which a current of carbonic acid (dried by passing through oil of vitriol, or over chloride of calcium) is flowing, and applying the heat of a spirit-lamp to the bulb. The metal will soon burn in the gas, which it robs of its oxygen, leaving the carbon as a black mass upon the bulb (fig. 86). The potash produced by the oxidation of the potassium enters into combination with another portion of the carbonic acid, forming a white mass of carbonate of potash, $3CO_2 + K_4 = 2(K_2O . CO_2) + C$. If slices of sodium be arranged in a test-tube in alternate layers with dried chalk (carbonate of lime), and strongly heated with a spirit-lamp, vivid combustion will ensue, and much carbon will be separated ($CaO . CO_2 + Na_4 = CaO + 2Na_2O + C$).

When the action of the sodium upon carbonic acid is moderated by employing it in the form of a mixture with pure dry sand, and by keeping the temperature below the boiling-point of mercury, oxalate of sodium is produced by the combination of the sodium with the elements of the carbonic acid, $Na_2 + 2CO_2 = Na_2C_2O_4$ (oxalate of sodium).

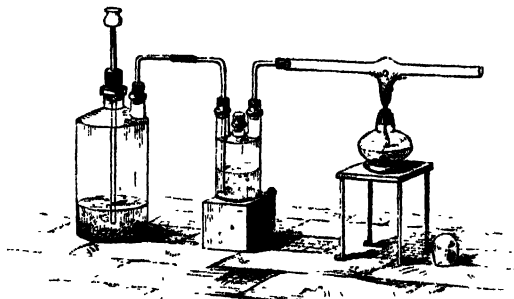


Fig. 86.

64. Carbonic oxide (CO = 28 parts by weight = 2 volumes).—Other metals, which are not endowed with so powerful an attraction for oxygen, do not carry the decomposition of carbonic acid to its final limit; thus, iron and zinc* at a high temperature will only deprive the gas of one-half of its oxygen, a result which may also be brought about at a red heat by carbon itself. If an iron tube filled with fragments of charcoal be heated to redness in a furnace (fig. 9), and carbonic acid gas be transmitted through it, it will be found, on collecting the gas which issues from the other extremity of the tube, that it has no longer the properties of carbonic acid, but that, on the approach of a taper, it takes fire, and burns with a beautiful blue lambent flame, similar to that which is often observed to play over the surface of a clear fire. Both flames, in fact, are due to the same gas, and in both cases this gas results from the same chemical change, for in the tube the carbonic acid yields half of its oxygen to the charcoal, both becoming converted into carbonic oxide; $CO_2 + C = 2CO$. In the fire, the carbonic acid is formed by the combustion of the carbon of the fuel in the oxygen of the air entering at the bottom of the grate; and this carbonic acid, in passing over the layer of heated carbon in the upper part of the fire, is partly converted into carbonic oxide, which

* Magnesium also reduces carbonic acid to carbonic oxide.

inflames when it meets with the oxygen in the air above the surface of the fuel, and burns with its characteristic blue flame, reproducing carbonic acid.

The carbonic oxide occupies twice the volume of the carbonic acid from which it was produced.

This conversion of carbonic acid into carbonic oxide is of great importance on account of its extensive application in metallurgic operations. It is often desirable, for instance, that a flame should be made to play over the surface of an ore placed on the bed or hearth of a reverberatory furnace (fig. 87). This object is easily attained when the coal affords a large

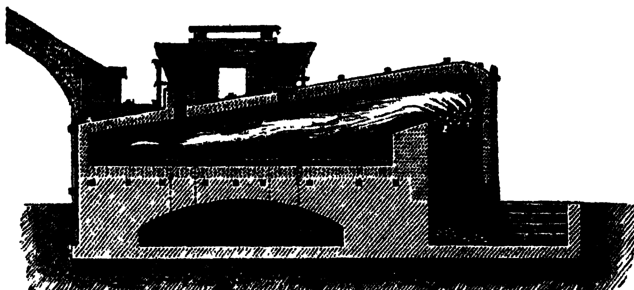


Fig. 87.—Reverberatory furnace for copper smelting.

quantity of inflammable gas; but with anthracite coal, which burns with very little flame, and is frequently employed in such furnaces, it is necessary to pile a high column of coal upon the grate, so that the carbonic acid formed beneath may be converted into carbonic oxide in passing over the heated coal above, and when this gas reaches the hearth of the furnace, into which air is admitted, it burns with a flame which spreads over the surface of the ore.

The attraction of carbonic oxide for oxygen is turned to account in removing that element from combination with iron in its ores, as will be seen hereafter.

Carbonic oxide is a gas of so poisonous a character that, according to Leblanc, one volume of it diffused through 100 volumes of air totally unfits it to sustain life; and it appears that the lamentable accidents which too frequently occur from burning charcoal or coke in braziers and chafing-dishes in close rooms, result from the poisonous effects of the small quantity of carbonic oxide which is produced and escapes combustion, since the amount of carbonic acid thus diffused through the air is not sufficient in many cases to account for the fatal result.

65. The knowledge of this poisonous character of carbonic oxide gave rise, a few years since, to considerable apprehension when it was proposed to employ this gas in Paris for purposes of illumination. The character of the flame of carbonic oxide would appear to afford little promise of its utility as an illuminating agent; but that it is possible so to employ it is easily demonstrated, by kindling a jet of the gas which has been passed through a wide tube containing a little cotton moistened with rectified coal naphtha (benzole), when it will be found to burn with a very luminous flame. The carbonic oxide destined to be employed for illuminating purposes was prepared by passing steam over red hot coke or charcoal, when

a highly inflammable gas was obtained, containing carbonic acid, carbonic oxide and hydrogen—



$$4H_2O + C_3 = CO_2 + 2CO + H_8.$$

Since neither hydrogen nor carbonic oxide burns with a luminous flame, this gas was next passed into a vessel containing red-hot coke, over which melted resin was allowed to trickle. The action of heat upon the resin gave rise to the production of vapours similar to that of the benzole employed in the above experiment, and which, in like manner, conferred considerable illuminating power upon the gas.

The decomposition of steam by red-hot carbon is also taken advantage of in order to procure a flame from anthracite coal when employed for heating boilers. The coal being burnt on *fish-bellied* bars, beneath which a quantity of water is placed, the radiated heat converts the water into steam, which is carried by the draught into the fire, where it furnishes carbonic oxide and hydrogen, both capable of burning with flame under the bottom of the boiler. The temperature of the bars is also thus reduced, so that they are not so much injured by the intense heat of the glowing fuel.

66. Carbonic oxide, unlike carbonic acid, is a permanent gas, and nearly insoluble in water. It is even lighter than air, its specific gravity being 0·967. In its chemical relations it is an indifferent oxide, that is, it has neither acid nor basic properties.

67. A very instructive process for obtaining carbonic oxide, consists in heating crystallised oxalic acid with three times its weight of oil of vitriol. If the gas be collected over water (fig. 88), and one of the jars be shaken with a little lime-water, the milkiness imparted to the latter will indicate abundance of carbonic acid; whilst, on removing the glass plate, and applying a light, the carbonic oxide will burn with its characteristic blue flame. The gas thus obtained is a mixture of equal volumes of carbonic oxide and carbonic acid gases. Crystallised oxalic acid is represented by the formula $C_2H_2O_4 . 2Aq.$, and if the water of crystallisation be left out of consideration, its decomposition may be represented by the equation—

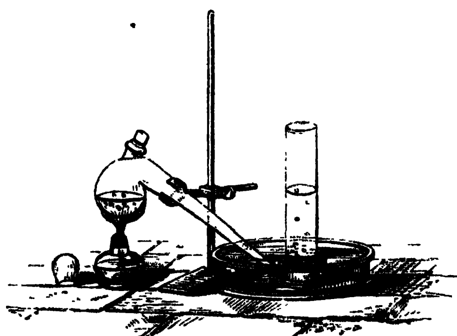
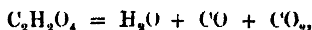


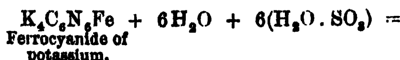
Fig. 88.



$$C_2H_2O_4 = H_2O + CO + CO_2,$$

the change being determined by the attraction of the oil of vitriol for water. To obtain pure carbonic oxide, the mixture of gases must be passed through a bottle containing solution of potash, to absorb the carbonic acid (fig. 89).

But pure carbonic oxide is much more easily obtained by the action of four parts of oil of vitriol upon one part of crystallised ferrocyanide of potassium (yellow prussiate of potash) at a moderate heat, the lamp being removed as soon as the effervescence begins to take place. Since the gas contains, especially at the commencement, small incidental quantities of sulphurous and carbonic acids, it must be passed through solution of potash if it be required perfectly pure. The chemical change which occurs in this process is expressed thus:—



$$\underset{\text{Ferrocyanide of potassium.}}{K_4C_6N_6Fe} + 6H_2O + 6(H_2O.SO_3) =$$



$$6CO + \underset{\text{Sulphate of potash.}}{2(K_2O.SO_3)} + \underset{\text{Sulphate of ammonia.}}{3[(NH_3)_2.H_2O.SO_3]} + \underset{\text{Sulphate of iron.}}{FeO.SO_3}$$

68. To demonstrate the production of carbonic acid during the combustion of carbonic oxide, a jar of the gas is closed with a glass plate, and after placing it upon the table, the plate is slipped aside and a little lime-water quickly poured into the jar. On shaking, no milkiness indicative of carbonic acid should be perceived. The plate is then removed, and the gas kindled. On replacing the plate and shaking the jar, an abundant precipitation of carbonate of lime will take place.

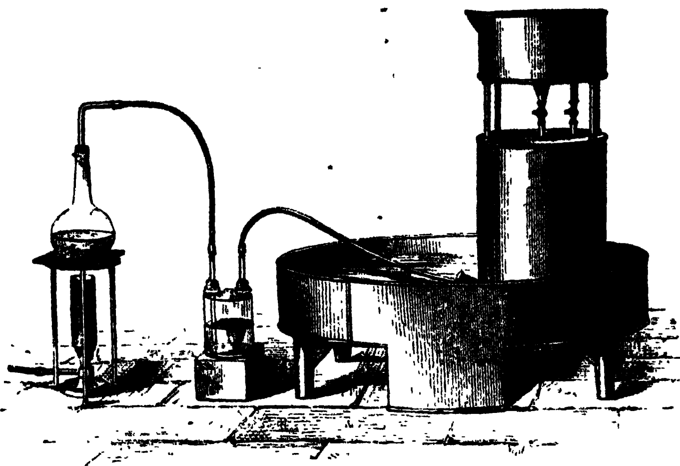


Fig. 89.—Preparation of carbonic oxide.

When carbonic oxide is passed through a red hot porcelain tube, a portion of it is decomposed into carbonic acid and carbon; and when the experiment is conducted without special arrangements, the carbonic oxide is reproduced as the temperature of the gas falls. But by passing through the centre of the porcelain tube a brass tube, through which cold water is kept running, the decomposition has been demonstrated by the deposition of carbon upon the cooled tube, and by collecting the carbonic acid formed.

Carbonic acid is also decomposed by intense heat into carbonic oxide and oxygen; but if these gases be allowed to cool down slowly in contact, they recombine. The gas drawn from the hottest region of a blast-furnace (*see* IRON), and rapidly cooled, so as to prevent recombination, was found to contain both carbonic oxide and oxygen.

By passing a pellet of phosphorus up into carbonic acid, over mercury, in a eudiometer and passing electric sparks for some days, the gas has been entirely decomposed, an equal volume of carbonic oxide being left.

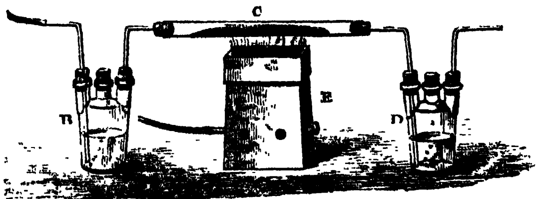


Fig. 90.—Reduction of oxide of copper by carbonic oxide.

The reducing action of carbonic oxide upon metallic oxides, at high temperatures, may be illustrated by passing the pure gas from a bag or gas-holder, first through

a bottle of lime-water (B, fig. 90), to prove the absence of carbonic acid, then over oxide of copper, contained in the tube C, and afterwards again through lime-water in D. When enough gas has been passed to expel the air, heat may be applied to the tube by the gauze-burner E, when the formation of carbonic acid will be immediately shown by the second portion of lime-water, and the black oxide of copper will be reduced to red metallic copper.

If precipitated peroxide of iron be substituted for oxide of copper, iron in the state of black powder will be left, and if allowed to cool in the stream of gas, will take fire when it is shaken out into the air, becoming reconverted into the peroxide (*iron pyrophorus*).

69. *Composition by volume of carbonic oxide and carbonic acid.*—When carbon burns in oxygen, the volume of the carbonic acid produced is exactly equal to that of the oxygen, so that one volume of oxygen furnishes one volume of carbonic acid gas, or a molecule (2 vols., *see* p. 36) of carbonic acid contains 2 vols. of oxygen.

When one volume of carbonic acid (containing one volume of oxygen) is passed over heated carbon, it yields two volumes of carbonic oxide; hence two volumes, or one molecule, of this gas contain one volume of oxygen.

Specific gravity (to H) of CO_2, *i.e.*, weight of one volume, .	22
Specific gravity (to H), or weight of one volume, of O, . .	16
Weight of carbon in one volume of CO_2, ...	6

Hence, a molecule, 2 vols. or 44 parts by weight, of CO_2, contains 12 parts by weight of carbon.

Specific gravity (to H), or weight of one volume, of CO, = 14	
Weight of two volumes of CO, ...	28
,, one volume of O, ...	16
Weight of carbon in two volumes (or one molecule) of CO,	12

70. The *atomic weight* of carbon is generally assumed to be 12, though, in consequence of the impossibility of determining the weight of one volume of carbon vapour by experiment, the chemist is compelled to surrender himself in this matter to the guidance of analogy and of purely theoretical considerations.

Compounds of Carbon and Hydrogen.

71. No two elements are capable of occurring in so many different forms of combination as carbon and hydrogen. The *hydrocarbons*, as their compounds are generally designated, include most of the inflammable gases which are commonly met with, and a great number of the essential oils, naphthas, and other useful substances. There is reason to believe that all these bodies, even such as are found in the mineral kingdom, have been originally derived from vegetable sources, and their history belongs, therefore, to the department of organic chemistry. The three simplest examples of such compounds will, however, be brought forward in this place, to afford a general insight into the mutual relations of these two important elements. Their names and composition are—

	Formulæ. (2 vols.)	Parts by Weight.	
		C	H
Acetylene, . .	C_2H_2	24	2
Marsh-gas, . .	CH_4	12	4
Olefiant gas, .	C_2H_4	24	4

72. *Acetylene.**—When very intensely heated, carbon is capable of combining with hydrogen to form acetylene. The requisite heat is procured by means of a powerful galvanic battery, to the terminal wires of which two pieces of dense carbon are attached, and the voltaic discharge is allowed to take place between them in an atmosphere of hydrogen. The experiment possesses little practical importance, because but little acetylene is formed in proportion to the force employed, but its theoretical interest is very great, since it is the first step in the production of organic substances by the direct synthesis of mineral elements ; acetylene (C_2H_2) being convertible into olefiant gas (C_2H_4), this last into alcohol (C_2H_6O), and alcohol into a very large number of organic products.

Acetylene is constantly found among the products of the incomplete combustion and destructive distillation of substances rich in carbon, hence it is always present in small quantity in coal-gas, and may be produced in abundance by passing the vapour of ether through a red-hot tube. The character by which acetylene is most easily recognised is that of producing a fine red precipitate in an ammoniacal solution of cuprous chloride (subchloride of copper.)

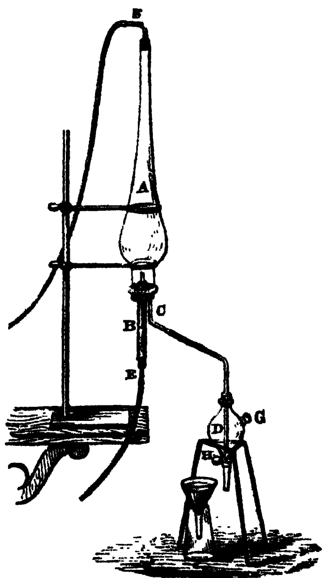


Fig. 91—Preparation of cuprous acetylide.

The most convenient process for preparing a quantity of this precipitate, is that in which the acetylene is produced by the imperfect combustion taking place when a jet of atmospheric air is allowed to burn in coal-gas.

An *adapter* (A, fig. 91) is connected at its narrow end with the pipe supplying coal-gas. The wider opening is closed by a bung with two holes, one of which receives a piece of brass tube (B) about three-quarters of an inch wide and seven inches long, and in the other is inserted a glass tube (C) which conducts the gas to the bottom of a *separating funnel* (D). The lower opening of the brass tube B is closed with a cork, through which passes the glass tube E connected with a gas-holder or bag containing atmospheric air. To commence the operation, the gas is turned on through the tube F, and when all air is supposed to be expelled, the tube E is with-

* Long known as *klumene*, having been obtained in 1836 by the action of water upon a compound containing carbon and potassium, produced during the preparation of that metal. The name acetylene is derived from the hypothetical radical acetyle (C_2H_3), to which acetylene bears the same relation as ethylene (C_2H_4) does to ethyle (C_2H_5).

drawn, together with its cork, and a light is applied to the lower opening of the brass tube, the supply of coal-gas being so regulated that it shall burn with a small flame at the end of the tube. A feeble current of air is then allowed to issue from the tube E, which is passed up through the flame into the adapter, where the jet of air continues to burn in the coal-gas,* and may be kept burning for hours with a little attention to the proportions in which the gas and air are supplied. A solution of subchloride of copper in ammonia is poured into the separating funnel through the lateral opening G, so that the imperfectly burnt gas may pass through it, when the cuprous acetylide is precipitated in abundance. When a sufficient quantity has been formed, or the copper solution is exhausted, the liquid is run out through the stop-cock (H) on to a filter, and replaced by a fresh portion. The precipitate may be rinsed into a flask provided with a funnel tube and delivery tube, allowed to subside, the water decanted from it, and some strong hydrochloric acid poured in through the funnel. On heating, the acetylene is evolved, and may be collected, either over water, or more economically in a small gas-bag, or in a mercurial gas-holder. To obtain a pint of the gas, as much of the moist copper precipitate is required as will measure about six ounces after settling down. Such a quantity may be prepared in about six hours.

A solution of cuprous chloride suitable for this experiment is conveniently prepared in the following manner: 500 grains of black oxide of copper are dissolved in seven measured ounces of common hydrochloric acid, in a flask, and boiled for about twenty minutes with 400 grains of copper in filings or fine turnings. The brown solution of cuprous chloride in hydrochloric acid thus obtained is poured into about three pints of water contained in a bottle; the white precipitate (cuprous chloride) is allowed to subside, the water drawn off with a siphon, and the precipitate rinsed into a twenty-ounce bottle, which is then quite filled with water and closed with a stopper. When the precipitate has again subsided, the water is drawn off, and four ounces of powdered chloride of ammonium are introduced, the bottle being again filled up with water, closed and shaken. The cuprous chloride is entirely dissolved by the chloride of ammonium, but would be reprecipitated, if more water were added. When required for the precipitation of acetylene, the solution may be mixed with about one-tenth of its bulk of strong ammonia (·880), which may be poured into the separating funnel (D) before the copper solution is introduced. Four measured ounces of the solution are sufficient for one charge, and yield, in three hours, about three measured ounces of the moist precipitate. The blue solution of ammoniacal cupric chloride, filtered from the red precipitate, may be rendered serviceable again by being shaken, in a stoppered bottle, with precipitated copper, prepared by reducing a solution of sulphate of copper, acidulated with hydrochloric acid, with a plate of zinc.

The red precipitate is said to consist chiefly of the oxide of a compound formed from acetylene by the substitution of Cu for H. This compound, C_2CuH, has been named by Berthelot *cupros-acetyle*, and may be regarded as the radical of a series of compounds. If but little free ammonia be present in the solution of cuprous chloride, the precipitate will contain the chloride of cupros-acetyle, $(C_2CuH)\,Cl$, as well as the oxide.

If the acetylene copper precipitate be collected on a filter, washed, and dried either by mere exposure to the air, or over oil of vitriol, it will be found to explode with some violence when gently heated, and it is said that the accidental formation of this compound in copper or brass pipes, through which coal-gas passes, has occasionally given rise to explosions.

When acetylene is passed through solution of nitrate of silver, a white curdy precipitate is formed, resembling chloride of silver in appearance, but insoluble in ammonia (which turns it yellow) as well as in nitric acid. It may be obtained by allowing the imperfectly burnt gas from the apparatus in fig. 91 to pass through nitrate of silver.

* It is advisable to attach a piece of thin platinum wire to the mouth of the glass tube to render the flame of the air more visible.

When this precipitate is washed and allowed to dry, it is violently explosive if heated, though it may be hammered without exploding.* A minute fragment of it placed on a glass plate, and touched with a red-hot wire, detonates loudly and shatters the glass like fulminate of silver. The explosive silver compound is said to contain the *oxide of argent-acetyle* $(C_2Ag_2H)_2O$, the chloride corresponding to it, $(C_2Ag_2H)\ Cl$, being precipitated when acetylene is passed through a solution of chloride of silver in ammonia. In a solution of hyposulphite of gold and sodium, acetylene gives a yellowish very explosive precipitate.

When potassium or sodium is heated in excess of acetylene, it is said that one half of the hydrogen is displaced by the metal, forming acetylide of potassium (C_2HK) or of sodium (C_2HNa), a portion of the acetylene being converted into olefiant gas (C_2H_4) by combination with the displaced hydrogen. When heated to dull redness, sodium completely decomposes acetylene, C_2Na_2 being obtained. Both these sodium compounds are violently decomposed by water, acetylene being reproduced.

The copious formation of acetylene during the imperfect combustion of ether is very readily shown by introducing a few drops of ether into a test-tube, adding a little ammoniacal solution of cuprous chloride, kindling the ether-vapour at the mouth of the tube, and inclining the latter so as to expose a large surface of the copper solution, when a lerge quantity of the red cuprous acetylide is produced. If nitrate of silver be substituted for the copper solution, the white precipitate of oxide of argent-acetyle is formed abundantly.

Acetylene has been found accompanying the vapour of hydrocyanate of ammonia produced by the action of ammonia on red-hot charcoal.

Acetylene is a colourless gas having a peculiar odour, recalling that of the geranium, which is always perceived where coal gas is undergoing imperfect combustion. It burns with a very bright smoky flame. Its most remarkable property is that of inflaming spontaneously when brought in contact with chlorine. If a jet of the gas be allowed to pass into a bottle of chlorine, it will take fire and burn with a red flame, depositing much carbon. When chlorine is decanted up into a cylinder containing acetylene standing over water, a violent explosion immediately takes place, attended with a vivid flash, and separation of a large amount of carbon; $C_2H_2 + Cl_2 = C_2 + 2HCl$.

When acetylene is passed into water, it is absorbed in sufficient quantity to impart a strong smell to the water, and to yield a decided precipitate with ammoniacal cuprous chloride and with nitrate of silver.

The action of heat upon acetylene is very remarkable and instructive, since it results in the formation of a complex body from one which is less complex in composition. When heated in a glass tube for half an hour to the point at which the glass began to soften, it was found to be reduced to one-fifth of its original volume, the greater portion of it having been converted into a liquid hydrocarbon, *styrole*, C_8H_8, hitherto obtained from the vegetable gum-resin known as storax. The remaining gas was chiefly hydrogen (a little carbon having separated) with a little olefiant gas. Benzole (C_6H_6) has been formed, in a similar way, from three molecules of acetylene. When heated in contact with coke or iron, the bulk of the acetylene is decomposed into its elements.

By suspending the acetylene copper precipitate in solution of ammonia, and heating with a little granulated zinc, Berthelot has induced the acetylene to combine with the (*nascent*) hydrogen to form olefiant gas (C_2H_4).

When a mixture of acetylene with nitrogen is acted on by a succession of electric sparks, hydrocyanic or prussic acid (HCN) is produced by their direct union.

* But if the precipitate is prepared from a slightly ammoniacal solution of nitrate of silver, it explodes violently under the hammer.

73. *Olefiant gas* (C_2H_4 = 28 parts by weight = 2 vols.)—This gas is found in larger quantity than acetylene, among the products of the action of heat upon coal and other substances rich in carbon, and it is one of the most important constituents of the illuminating gases obtained from such materials.

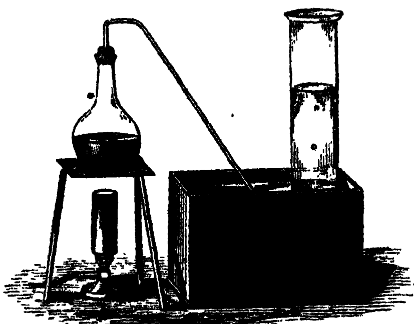


Fig. 92.—Preparation of olefiant gas.

Olefiant gas may readily be prepared by the action of strong sulphuric acid (oil of vitriol, $H_2O \cdot SO_3$) upon alcohol (spirit of wine C_2H_6O).

Two measures of oil of vitriol are introduced into a flask (fig. 92), and one measure of alcohol is gradually poured in, the flask being agitated after each addition of the acid; much heat is evolved, and there would be danger in mixing large volumes suddenly.* On applying a moderate heat, the liquid will darken in colour, effervescence will take place, and the gas may be collected in jars filled with water. When the mixture has become thick, and the evolution of the gas is slow, the end of the tube must be removed from the water and the lamp extinguished. Three measured ounces of spirit of wine generally give about 500 cubic inches of olefiant gas.

The gas will be found to have a very peculiar odour, in which that of ether and of sulphurous acid are perceptible. One of the jars may be closed with a glass plate, and placed upon the table with its mouth upwards; on the approach of a flame the gas will take fire, burning with a bright white flame characteristic of olefiant gas, and seen to best advantage when, after kindling the gas, a stream of water is poured down into the jar in order to displace the gas (fig. 93).

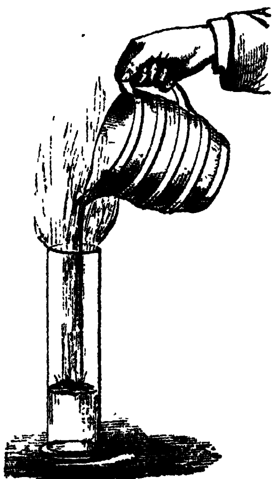


Fig. 93.

Another jar of the gas may be well washed by transferring it repeatedly from one jar to another under water, a little solution of potash may then be poured into it, and the jar violently shaken, its mouth being covered with a glass plate; the potash will remove all the sulphurous acid, and the gas will now exhibit the peculiar faint odour which belongs to olefiant gas.

The purified gas may be transferred, under water, to another jar, kindled, and allowed to burn out; if a little lime-water be then shaken in the jar, its turbidity will indicate the presence of carbonic acid, which is produced, together with water, when olefiant gas burns in air: $C_2H_4 + O_6 = 2CO_2 + 2H_2O$.

On comparing the composition of olefiant gas (C_2H_4) with that of alcohol (C_2H_6O), it is evident that the former may be supposed to be produced from the latter by the abstraction of a molecule of water (H_2O) which is removed by the sulphuric acid, though other secondary changes take place, resulting in the separation of carbonaceous matter and the production of sulphurous acid. A more complete explanation of the action of sulphuric acid upon alcohol must be reserved for the chemical history of this compound.

* If methylated spirit be employed, the mixture will have a dark red-brown colour.

Olefiant gas derives its name from its property of uniting with chlorine and bromine to form oily liquids, a circumstance which is applied for the determination of the proportion of this gas present in coal-gas, upon which great part of the illuminating value of coal-gas depends. The compound with chlorine ($C_2H_4Cl_2$) is known as *Dutch liquid*, having been discovered by Dutch chemists, and is remarkable for its resemblance to chloroform in odour.

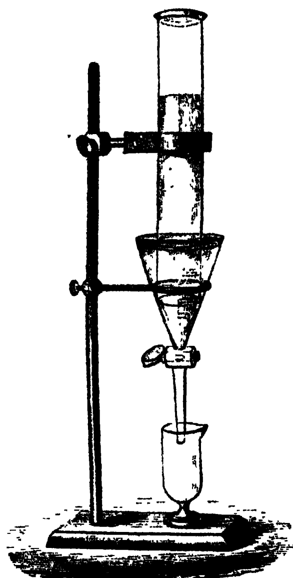


Fig. 94.

To exhibit the formation of Dutch liquid, a quart cylinder (fig. 94) is half filled with olefiant gas, and half with chlorine, which is rapidly passed up into it, from a bottle of the gas, under water. The cylinder is then closed with a glass plate, and supported with its mouth downwards under water in a *separating funnel* furnished with a glass stop-cock. The volume of the mixed gases begins to diminish immediately, drops of oil being formed upon the side of the cylinder and the surface of the water. As the drops increase, they fall to the bottom of the funnel. Water must be poured into the funnel to replace that which rises into the cylinder, and when the whole of the gas has disappeared, the oil may be drawn out of the funnel through the stop-cock into a test-glass, in which it is shaken with a little potash to absorb any excess of chlorine. The fragrant odour of the Dutch liquid will then be perceived, especially on pouring it out into a shallow dish.

In applying this principle to the measurement of the illuminating hydrocarbons in coal-gas, daylight must be excluded, or an error would be caused by the union of the free hydrogen with the chlorine or bromine. The *bromine test* may be applied in the tube represented in fig. 95. The gas to be examined is measured over water in the divided limb *a*, with due attention to temperature and pressure; the tube being held perpendicularly, the limb *b* will remain filled with water, so that gas cannot escape nor air enter. A drop or two of bromine is poured into this limb, which is then depressed beneath the water in the pneumatic trough, and closed by the stopper *c*. On shaking the gas with the water and bromine, the latter will absorb the illuminating hydrocarbons, and if the tube be again opened under water, the volume of the gas in *a* will be found to have diminished, and the diminution gives an approximate estimate of the olefiant gas and other illuminating hydrocarbons.



Fig. 95.

A very instructive experiment consists in filling a three-pint cylinder one-third full of olefiant gas, then rapidly filling it up, under water, with two pints of chlorine, closing its mouth with a glass plate, shaking it to mix the gases, slipping the plate aside and applying a light, when the mixture burns with a red flame which passes gradually down the cylinder, and is due to the combination of the hydrogen with the chlorine, the whole of the carbon being separated in the solid state—



$$C_2H_4 + Cl_4 = 4HCl + C_2.$$

When olefiant gas is subjected to the action of high temperatures, as by passing through heated tubes, one portion is decomposed into marsh-gas (CH_4) with separation of carbon, whilst another portion yields acetylene (CH_2) and hydrogen; these decompositions will be found to be of great importance in the manufacture of coal-gas.

The action of heat upon olefiant gas is most conveniently shown by exposing it to the spark from an induction coil.

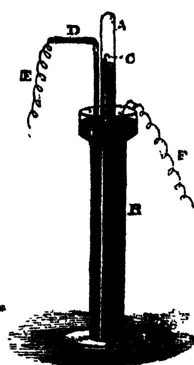
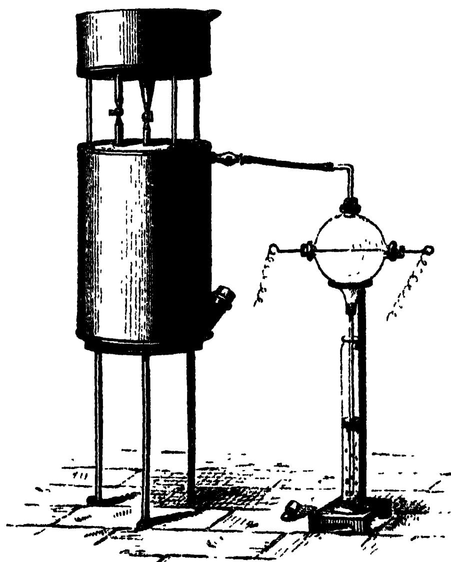


Fig. 96.

The gas is confined in a tube (A, fig. 96) which is placed in a cylindrical jar (B) containing mercury. Through the mercury passes a copper wire (C) thrust through a glass tube (D) to insulate it from the mercury; this wire is connected with one of the wires (E) from the induction coil, whilst the other (F) is allowed to dip into the mercury contained in the cylinder. On putting the coil in action (with two or three cells of Grove's battery), the spark will pass between the extremity (C) of the insulated copper wire and the surface of the mercury in the tube, decomposing the olefiant gas in its passage, and causing a separation of carbon, which sometimes forms a conducting communication, and allows the current to pass without a spark. This may be obviated by reversing the current, or by gently shaking the tube.

The olefiant gas will expand to nearly twice its former volume, so that the tube will gradually rise in the mercury, but the same distance may always be maintained for the passage of the spark.

To show the production of acetylene, another arrangement will be found convenient (fig. 97). A globe with four necks is employed; through two of these necks are passed, air-tight with perforated corks, the copper wires connected with the induction coil. A third neck receives a tube, conveying olefiant gas from a gas-holder, whilst from the fourth proceeds a tube dipping to the bottom of a small cylinder. When the whole of the air has been displaced by olefiant gas, a solution of subchloride of copper in ammonia is poured into the cylinder, and the gas allowed to bubble through it, when the absence of acetylene will be shown by there being no red compound formed. As soon, however, as the spark is passed, the red precipitate will appear, and, in a very few minutes, a large quantity will be deposited. Coal-gas may be employed instead of olefiant gas, but of course less of the copper-compound will be obtained.


Fig. 97.—Preparation of cuprous acetylide from olefiant gas.

74. *Marsh-gas*, or *light carburetted hydrogen* (CH_4 = 16 parts by weight = 2 vols.)—Unlike acetylene and olefiant gas, this hydrocarbon is found in nature, being produced wherever vegetable matter is undergoing decomposition in the presence of moisture. The bubbles rising from stagnant pools, when collected and examined, are found to contain marsh-gas mixed with carbonic acid, and there is reason to believe that these two gases represent the principal forms in which the hydrogen and oxygen respectively were separated from wood during the process of its conversion into coal. This would account for the constant presence of

this gas in the coal-formations, where it is usually termed *fire-damp*. It is occasionally found pent up under pressure between the layers of coal, and the pores of the latter are sometimes so full of it that it may be seen rising in bubbles when the freshly hewn coal is thrown into water. Perhaps a similar origin is to be ascribed to the liquid hydrocarbons chemically similar to marsh-gas, which are found so abundantly in Pennsylvania and Canada, and are known by the general name of *petroleum*.

Marsh-gas is obtained artificially by the following process:—

500 grains of dried acetate of soda are finely powdered, and mixed, in a mortar, with 200 grains of solid hydrate of potash, and 300 grains of powdered quicklime (or with 500 grains of the mixture of hydrate of lime and hydrate of soda, which is sold as *soda-lime*). The mixture is heated in a Florence flask (or better, a copper tube, for the alkali corrodes the glass), and the gas collected over water (fig. 98).

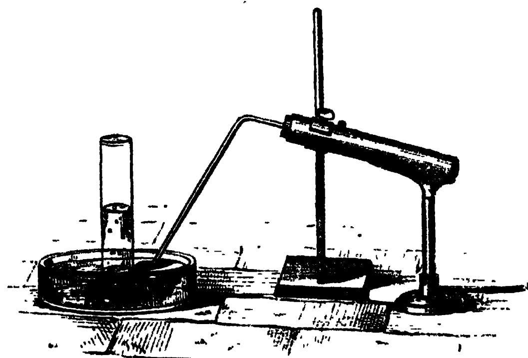
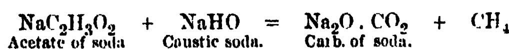


Fig. 98.—Preparation of marsh-gas.

The decomposition will be evident from the following equation:



$$\underset{\text{Acetate of soda}}{NaC_2H_3O_2} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Carb. of soda.}}{Na_2O \cdot CO_2} + CH_4$$

The marsh-gas will be easily recognised by its burning with a pale illuminating flame, far inferior in brilliancy to those of olefiant gas and acetylene, but unattended with smoke.

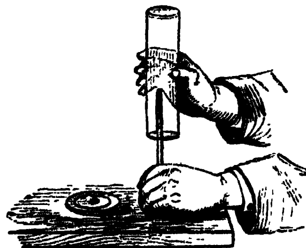
The properties of this gas deserve a careful study, on account of the frequent fatal explosions to which it gives rise in coal-mines, where it is often found accumulated under pressure, and discharging itself with considerable force from the fissures or *blowers* made in hewing the coal. Marsh-gas has no characteristic smell like coal-gas, and the miner thence receives no timely warning of its presence; it is much lighter than air (sp. gr. 0·5596), and therefore very readily diffuses* itself (page 16) through the air of the mine, with which it forms an explosive mixture as soon as it amounts to one-eighteenth of the volume of the air. The gas issuing from the blower would burn quietly on the application of a light, since the marsh-gas is not explosive unless mixed with the air, when a large volume of the gas is burnt in an instant, causing a sudden evolution

* *Ansell's fire-damp indicator* is an apparatus in which the high rate of diffusion of marsh-gas is taken advantage of in order to detect its presence in the air of mines. The experiment described at page 18 illustrates its principle.

of a great deal of heat, and a consequent sudden expansion or explosion exerting great mechanical force. The most violent explosion takes place when one volume of marsh-gas is mixed with two volumes of oxygen, since this quantity is exactly sufficient to effect the complete combustion of the carbon and hydrogen of the gas, and therefore to evolve the greatest amount of heat: $CH_4 + O_4 = CO_2 + 2H_2O$. The calculated pressure exerted by the exploding mixture of marsh-gas and oxygen amounts to 37 atmospheres, or 555 lbs. upon the square inch. Since air contains one-fifth of its volume of oxygen, it would be necessary to employ ten volumes of air to one volume of marsh-gas in order to obtain perfect combustion, but the explosion will be much less violent on account of the presence of the eight volumes of inert nitrogen, the calculated pressure exerted by the explosion being only 14 atmospheres, or 210 lbs. on the square inch. Of course, if more air is employed, the explosion will be proportionally weaker, until, when there are more than eighteen volumes of air to each volume of marsh-gas, the mixture will be no longer explosive, but will burn with a pale flame around a taper immersed in it. The carbonic acid resulting from the explosion is called by miners the *after-damp*, and its effects are generally fatal to those who may have escaped death from the explosion itself.

Fortunately, marsh-gas requires a much higher temperature to inflame it than most other inflammable gases; thus a solid body at an ordinary red heat does not kindle the gas, contact with flame, or with a body heated to whiteness, being required to ignite it.

If two strong gas cylinders be filled, respectively, with mixtures of 2 vols. hydrogen with 1 vol. oxygen, and of 1 vol. marsh-gas and 2 vols. oxygen, it will be found, on holding them with their mouths downwards, and inserting a red-hot iron bar (fig. 99), that the marsh-gas mixture will not explode, but if the bar be transferred at once to the hydrogen mixture, explosion will take place. A lighted taper may then be used to explode the marsh-gas and oxygen.


Fig. 99.

Coal-gas, although answering very well for many illustrations of the properties of marsh-gas, cannot be used in this experiment, since some of its constituents inflame at a far lower temperature.

In consequence of the high temperature required to inflame the mixture of marsh-gas and air, it is necessary that the mixture be allowed to remain for an appreciable time in contact with the flame before its particles are raised to the igniting point. It was on this principle that Stephenson's original safety lamp was constructed, the flame being surrounded with a tall glass chimney, the rapid draught through which caused the explosive mixture to be hurried past the flame without igniting.

To illustrate this, a copper funnel holding about two quarts (fig. 100) is employed, the neck of which has an opening of about ¼ inch in diameter. The funnel being placed mouth downwards in the pneumatic trough, the orifice is closed with the finger, and half a pint of coal-gas passed up into the funnel. The latter is now raised from the water, so that it may become entirely filled with air. By depressing the funnel to a considerable depth in the water, the aperture being still closed by the finger, the mixture will be confined under considerable pressure, and if a lighted taper be held to the aperture, and the finger removed, it will be found that the mixture sweeps past the flame without exploding, until the water has reached the

same level in the funnel as in the trough, when the gas comes to rest and explodes with great violence.

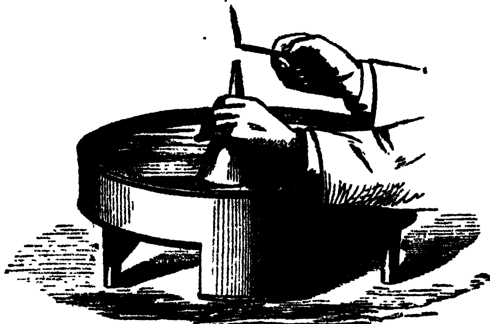


Fig. 100.

Davy's safety lamp (fig. 101) is an application of the principle that ignited gas (*flame*) is extinguished by contact with a large surface of a good conductor of heat, such as copper or iron.

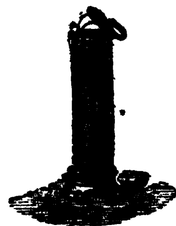


Fig. 101.—Davy lamp.

If a thin copper wire be coiled round into a helix, and carefully placed over the wick of a burning taper (fig. 102), the flame will be at once extinguished, its heat being so rapidly transmitted along the wire that the temperature falls below the point at which the combustible gases enter into combination with oxygen, and therefore the combustion ceases. If the coil be heated to redness in a spirit-lamp flame before placing it over the wick, it will not abstract the heat so readily, and will not extinguish the flame. If a copper tube were substituted for the coiled wire, the same result would be obtained, and by employing a number of tubes of very small diameter, so that the metallic surface may be very large in proportion to the volume of ignited gas, the most energetic combustion may be arrested, as in the case of *Hemming's safety jet*, which consists of a brass tube tightly stuffed with thin copper wires so as to leave very narrow passages, thus rendering it impossible for the oxyhydrogen flame at the jet to pass back and ignite the mixture in the reservoir.

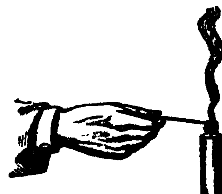


Fig. 102.

It is evident that the exposure of a large extent of cooling surface to the action of the flame, may be effected either by increasing the length or by diminishing the width of the metallic tubes, so that wire gauze, which may be regarded as a collection of very short tubes, will form an effectual barrier to flame, provided that it has a sufficient number of meshes to the inch.

If a piece of iron wire gauze, containing about 800 meshes to the square inch, be depressed upon a flame, it will extinguish that portion with which it is in contact, and the combustible gas which escapes through the gauze may be kindled by a lighted match held on the upper side. By holding the gauze two or three inches above a gas jet, the gas may be lighted above it without communicating the flame to the burner itself.

When blazing spirit is poured upon a piece of wire gauze (fig. 103), the flame will remain upon the gauze, and the extinguished spirit will pass through. A little benzole or turpentine may be added to the spirit, so that its flame may be more visible at a distance.

The safety lamp is an oil lamp, the flame of which is surrounded by a cage of iron wire gauze, having 700 or 800 meshes in the square inch, and made double at the top where the heat of the flame chiefly plays. This cage is protected by stout iron wires attached to a ring for suspend-

ing the lamp. A brass tube passes up through the oil reservoir, and in this there slides, with considerable friction, a wire bent at the top, so that the wick may be trimmed without taking off the cage.

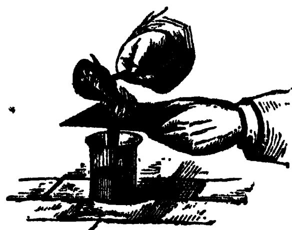


Fig. 103.

If this lamp be suspended in a large jar, closed at the top with a perforated wooden cover (A, fig. 104), and having an aperture (B) below, through which coal-gas may be admitted, the lamp will burn, of course in the ordinary way; but if the gas be allowed to pass slowly into the jar, the flame will be seen to waver, to elongate itself very considerably, and will be ultimately extinguished, when the wire cage will be seen to be filled with a mixture of coal-gas and air burning tranquilly within the gauze, which prevents the flame from passing to ignite the explosive atmosphere surrounding the lamp; that an explosive mixture really fills the jar may be readily ascertained by introducing, through an aperture (C) in the cover, the unprotected flame of a taper, when an explosion will take place.

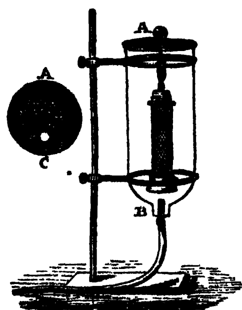


Fig. 104.

This experiment illustrates the action of the Davy lamp in a mine which contains fire-damp, and makes it evident that this lamp would afford complete protection if carefully used. It would obviously be unsafe to allow the lamp to remain in the explosive mixture when the cage is filled with flame, for the gauze would either become sufficiently heated to kindle the surrounding gas, or would be oxydised and eaten into holes, which would allow the passage of the flame. Nor should the lamp be exposed to a very strong current, which might possibly be able to carry the flame through the meshes.

The great defect of the Davy lamp is that it does not afford more than a glimmering light, so that even if the miners were prohibited from employing any candles, they would (and experience has proved that they do) remove the wire cage at all risks. The lamp has been modified so as partially to remove this defect, by substituting glass or talc for some portions of the wire gauze. It is now usual, however, to employ the Davy lamp merely in order to test the state of the air in the different parts of the mine; for this purpose the *firemen* descend before the commencement of work every morning, and examine with their safety lamps every portion of the mine, giving warning to the miners not to approach those parts in which any accumulation of fire-damp (or technically, "sulphur") is perceived. The miners then work with naked candles, and it appears to be not unusual to see a blue flame (or *corpse light*) playing around the candles, so that the miners may become accustomed to regard with little concern the very indication which shows that the quantity of fire-damp is only a little below that required to form an explosive mixture. Whenever naked flames are used in the mine there must always be great risk; in most seams of coal there are considerable accumulations of fire-damp; when a fissure is made, the gas escapes very rapidly from the *blower*, and the air in its vicinity may soon become converted into an explosive mixture. In mines where small quantities of fire-damp are known to be continually escaping from the coal, ventilation is depended upon in order to dilute the gas with so large a volume of air that it is no longer explosive, and finally to sweep it out of the mine; but it has occasionally happened that the ventilation has been interfered with by a door having

been left open in one of the galleries, or by a passage having been obstructed through the accidental falling in of a portion of the coal, and an explosive mixture has then been formed.

STRUCTURE OF FLAME.

75. The consideration of the structure and properties of ordinary flames is necessarily connected with the history of olefiant gas and marsh-gas. Flame may be defined as gaseous matter, heated to the temperature at which it becomes visible, or emits light. Solid particles begin, for the most part, to emit light when heated to about 1000° F.; but gases, on account of their greater expansibility, must be raised to a far higher temperature, and hence the point of visibility is seldom attained, except by gases which are themselves combustible, and therefore capable of producing, by their own combination with atmospheric oxygen, the requisite degree of heat. The presence of a combustible gas (or vapour), therefore, is one of the conditions of the existence of flame; a diamond, or a piece of thoroughly carbonised charcoal, will burn in oxygen with a steady glow, but without flame, since the carbon is not capable of conversion into vapour, while sulphur burns with a voluminous flame, in consequence of the facility with which it assumes the vaporous condition. It will be observed, moreover, that in the case of a non-volatile combustible, the combination with oxygen is confined to the surface of contact, whilst in the flame of a gas or vapour, the combustion extends to a considerable depth, the oxygen intermingling with the gaseous fuel.

Flames may be conveniently spoken of as *simple* or *compound*, accordingly as they involve one or more phenomena of combustion; thus, for example, the flames of hydrogen and carbonic oxide are simple, whilst those of marsh-gas and olefiant gas are compound, since they involve both the conversion of hydrogen into water and of carbon into carbonic acid.

It is obvious that simple flames must be hollow in ordinary cases, such as that of a gas issuing from a tube into the air, the hollow being occupied by the combustible gas to which the oxygen does not penetrate.

All the flames which are ordinarily turned to useful account are compound flames, and involve several distinct phenomena. Before examining these more particularly, it will be advantageous to point out the conditions which regulate the luminosity of flames.

In order that a flame may emit a brilliant light, it is essential that it should contain particles which, either from their own nature, or from the conditions under which they are placed, do not admit of indefinite expansion by the heat of the flame, but are capable of being heated to *incandescence*. Thus, the flame of the oxyhydrogen blowpipe (p. 38) emits a very pale light, but if the mixture of oxygen and hydrogen be restrained from expanding when fired, as in the Cavendish eudiometer (p. 32), it gives a bright flash; or if the flame be directed upon some solid body little affected by heat, such as lime, the light is very intense.

Phosphorus and arsenic burn with very luminous flames, in consequence of the formation of very dense vapours of phosphoric and arsenious acids during the combustion; the density of the vapours being here attended with the same result as that produced by the restrained expansion of the steam formed in the Cavendish eudiometer.

It is not necessary that the incandescent matter should be a product of the combustion; any extraneous solid in a finely divided state will

confer illuminating power upon a flame. Thus, the flame of hydrogen may be rendered highly luminous by burning a piece of phosphorus in its vicinity, so that the clouds of phosphoric acid may pass through the flame, or by blowing a little very fine charcoal powder into it, from the bottle represented in fig. 105.



Fig. 105.

The luminosity of all ordinary flames is due to the presence of highly heated carbon in a state of very minute division, and it remains to consider the changes by which this finely divided carbon is separated in the flame.

A candle, a lamp, and a gas-burner, exhibit contrivances for procuring light artificially in different degrees of complexity, the candle being the most complex of the three. When a new candle is lighted, the first portion of the wick is burnt away until the heat reaches that part which is saturated with the wax or tallow of which the candle is composed; this wax or tallow then undergoes destructive distillation, yielding a variety of products, among which olefiant gas is found in abundance. The flame furnished by the combustion of these products melts the fuel around the base of the wick, through which it then mounts by capillary attraction, to be decomposed in its turn, and to furnish fresh gases for the maintenance of the flame. In a lamp, the fuel being liquid at the commencement, the process of fusion is dispensed with; and in a gas-burner, where the fuel is supplied in a gaseous form, the process of destructive distillation has been already carried on at a distance. It will be seen, however, that the final result is similar in all three cases, the flame being maintained by such gases as acetylene, marsh-gas, and olefiant gas, arising from the destructive distillation of wax, tallow, oil, coal, &c.



Fig. 106.

On examining an ordinary flame, that of a candle, for instance, it is seen to consist of three concentric cones (fig. 106), the innermost, around the wick, appearing almost black, the next emitting a bright white light, and the outermost being so pale as to be scarcely visible in broad daylight.

The dark innermost cone consists merely of the gaseous combustible to which the air does not penetrate, and which is therefore not in a state of combustion.

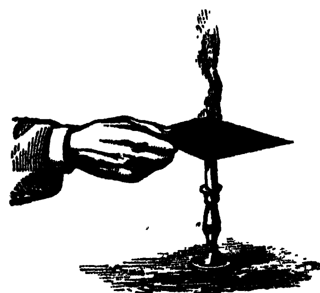


Fig. 107.

The nature of this cone is easily shown by experiment: a strip of cardboard held across the flame near its base will not burn in the centre where it traverses the innermost cone; a piece of wire gauze depressed upon the flame near the wick (fig. 107) will allow the passage of the combustible gas, which may be kindled above it. The gas may be conveyed out of the flame by means of a glass tube inserted into the innermost cone, and may be kindled at the other extremity of the tube, which should be inclined downwards (fig. 108).

A piece of phosphorus in a small spoon held in the interior of the flame of a spirit-lamp, will melt and boil, but will not burn unless it be removed from the flame, and may then be extinguished by replacing it in the flame.

The combustible gas from the interior of a flame may be collected in a flask (fig. 109) furnished with two tubes, one of which (A) is drawn out to a point for

insertion into the flame, whilst the other (B), which passes to the bottom of the flask, is bent over and prolonged by a piece of vulcanised tubing, so that it may act as a

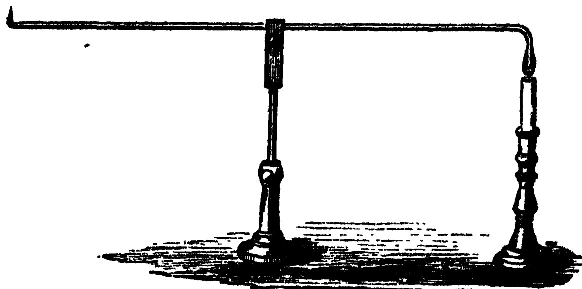


Fig. 108.

siphon. The flask is filled up with water, the jet inserted into the interior of a flame, and the siphon set running by exhausting it with the mouth. As the water flows out through the siphon, the gas is drawn into the flask, and after removing the tube from the flame, the gas may be expelled by blowing down the siphon tube, and may be burnt at the jet. When a candle is used for this experiment, some solid products of destructive distillation will be found condensed in the flask.

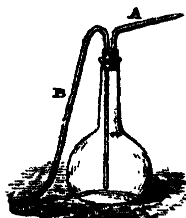


Fig. 109.

In the second or luminous cone, combustion is taking place, but it is by no means perfect, being attended by the separation of a quantity of carbon, which confers luminosity upon this part of the flame. The presence of free carbon is shown by depressing a piece of porcelain upon this cone, when a black film of soot is deposited. The liberation of the carbon is due to the decomposition of the olefiant gas and similar hydrocarbons by the heat, which separates the carbon from the hydrogen, and this latter, undergoing combustion, evolves sufficient heat to raise the separated carbon to a white heat, the supply of air which penetrates into this portion of the flame being insufficient to effect the combustion of the whole of the carbon.

Some very simple experiments will illustrate the nature of the luminous portion of flame.

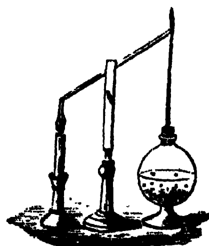


Fig. 110.

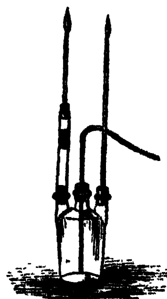


Fig. 111.

Over an ordinary candle flame (fig. 110) a tube may be adjusted so as to convey the finely divided carbon from the luminous part of the flame into the flame of

hydrogen, which will thus be rendered as luminous as the candle flame, the dark colour of the carbon being apparent in its passage through the tube.

A bottle furnished with two straight tubes (fig. 111) is connected with a reservoir of hydrogen. One of the tubes is provided with a small piece of wider tube containing a tuft of cotton wool. On kindling the gas at the orifice of each tube, no difference will be seen in the flames until a drop of benzole (C_6H_6) is placed upon the cotton, when its vapour, mingling with the hydrogen, will furnish enough carbon to render the flame brilliantly luminous.

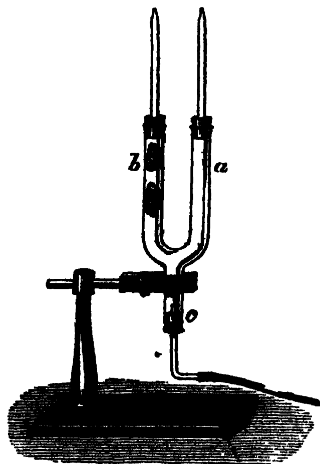


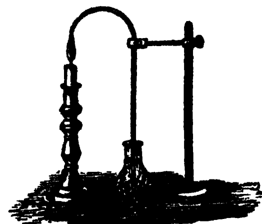
Fig. 112.

Fig. 112 shows a more convenient apparatus for the same purpose; the hydrogen being passed in through *c*, burns from the tube *a* with a non-luminous flame, and from the tube *b*, after passing over a piece of cotton, moistened with benzole, with a luminous flame.

The pale outermost cone, or *mantle*, of the flame, in which the separated carbon is finally consumed, may be termed the cone of perfect combustion, and is much thinner than the luminous cone, the supply of air to this external shell of flame being unlimited, and the combustion therefore speedily effected.

The mantle of the flame may be rendered more visible by burning a little sodium near the flame, when the mantle is tinged strongly yellow.

By means of a siphon about one-third of an inch in diameter (fig. 113), the nature of the different portions of an ordinary candle flame may be very elegantly shown. If the orifice of the siphon be brought just over the extremity of the wick, the combustible gases and vapours will pass through it, and may be collected in a small flask, where they can be kindled by a taper. On raising the orifice into the luminous portion of the flame, voluminous clouds of black smoke will pour over into the flask, and if the siphon be now raised a little above the point of the flame, carbonic acid can be collected in the flask, and may be recognised by shaking with lime-water.


Fig. 113.

The reciprocal nature of the relation between the combustible gas and the air which supports its combustion may be illustrated in a striking manner by burning a jet of air in an atmosphere of coal-gas.

A quart glass globe with three necks is connected at A (fig 114) with the gas-pipe by a vulcanised tube. The second neck (B), at the upper part of the globe, is connected by a short piece of vulcanised tube with a piece of glass tube about ¼ inch wide, from which the gas may be burnt. Into the third and lowermost neck is inserted, by means of a cork, a thin brass tube, C (an old cork-borer), about ¼ inch in diameter. When the gas is turned on, it may be lighted at the upper neck; and if a lighted match be then quickly thrust up the tube C, the air which enters it will take fire and burn inside the globe.

A very inexpensive apparatus for this purpose may be constructed from a common Florence oil-flask. By applying a blowpipe flame at A (fig. 115), so as to heat to whiteness a spot as large as a threepenny-piece, and quickly blowing into the neck of the flask, the heated portion of the glass may be made to bulge out. A similar protuberance is then to be formed at B. A sharp-pointed flame is directed upon A, and the glass burst by blowing into the flask whilst it is still exposed to the flame. By fusing the edges of the hole thus produced, and turning them outwards with the end of a file, a short neck may be formed capable of receiving a cork. When this is cool, it is closed with a cork, and a second similar neck is produced at B.

From this review of the structure of flame, it is evident that, in order to secure a flame which shall be useful for illumination, attention must

be paid to the supply of oxygen (or air), and to the composition of the fuel employed. The use of the chimney of an Argand burner (fig. 116)

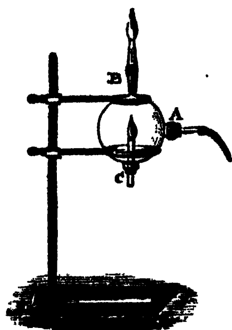


Fig. 114.—Air burning in coal-gas.

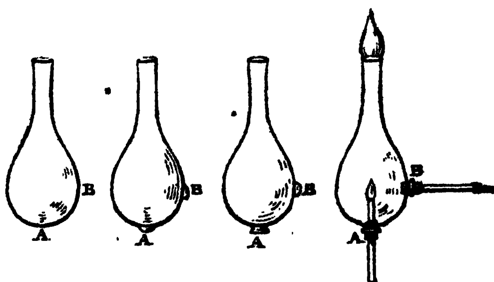


Fig. 115.—To make a three necked-flask.

affords an instance of the necessity for attention to the proper supply of air. Without the chimney, the flame is red at the edges and smoky, for the supply of air is not sufficient to consume the whole of the carbon which is separated, and the temperature is not competent to raise it to a bright white heat, defects which are remedied as soon as the chimney is placed over it, and the rapidly-ascending heated column of air draws in a liberal supply beneath the burner, as indicated by the arrows.

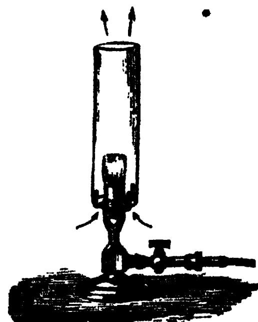


Fig. 116.—Argand burner.

By using two chimneys, and causing the air to pass down between them, so as to be heated to about 500° F. before reaching the flame, an equal amount of light may be obtained from a much smaller supply of gas.

The smokeless gas-burners employed in laboratories and kitchens exhibit the result of mixing the gas with a considerable proportion of air before burning it, the luminous part of the flame then entirely disappearing, with great augmentation of the temperature of the flame, since the carbon is burnt simultaneously with the hydrogen.

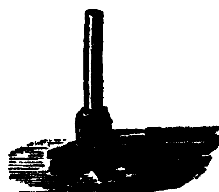
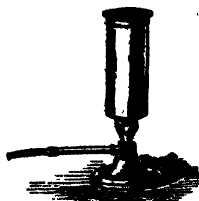


Fig. 117.—Bunsen's burner.

The most efficient burner of this kind (*Bunsen's burner*, fig. 117) is that in which the gas is conveyed into a wide tube, at the base of which there are four large holes for the admission of air. When a good supply of gas is turned on, a quantity of air is drawn in through the lower apertures, and the mixture of air and gas may be kindled at the orifice of the wide tube, its rapid motion preventing the flame from passing down within the tube. This tube is sometimes surmounted by a rosette burner to distribute the flame. By closing the air-holes with the fingers, a luminous flame is at once produced.

The principle of this burner has been applied for testing the illuminating value of gas, by measuring the quantity of air which must be supplied to a flame consuming a given quantity of gas, in order to destroy the luminosity, the illuminating value being proportional to the quantity of air which is necessary for this purpose.

The *gauze burner* (fig. 118) consists of an open cylinder surmounted by wire gauze. When this is placed over the gas burner, a supply of air is drawn in at the bottom by the ascending stream of gas, and the mixture burns above the gauze with a very hot smokeless flame, the metallic meshes preventing the flame from passing down to the gas below.


Fig. 118.—Gauze burner.

The luminosity of a flame is materially affected by the pressure of the atmosphere in which it burns, a diminution of pressure causing a loss of illuminating power. If the light of a given flame burning in the air when the barometer stands at 30 inches be represented by 100, each diminution of one inch in the height of the barometer will reduce the luminosity by five; and conversely, when the barometer rises one inch, the luminosity will be increased by five. This is not due to any difference in the rate of burning, which remains pretty constant, but to the more complete interpenetration of the rarefied air and the gases composing the flame, giving rise to the separation of a smaller quantity of incandescent carbon. In air at a pressure of 120 inches of mercury, the flame of alcohol is highly luminous, the high density of the air discouraging the intermixture of the flame-gases with it, and thus allowing the separation of a portion of carbon.

In considering the influence exerted by the composition of the fuel upon the character of its flame, it will be necessary to bear in mind that some kinds of fuel consist of carbon and hydrogen only, whilst others contain a considerable proportion of oxygen.

The following table exhibits the composition of some of the principal substances concerned in producing ordinary illuminating flames :—

Fuel.	Formula.	Carbon.	Hydrogen.	Oxygen.
Marsh-gas,	CH_4	30	10	
Olefiant gas,	C_2H_4	60	10	
Paraffine,	C_xH_{2x+2}	30	10	
Turpentine,	$C_{10}H_{16}$	75	10	
Benzole,	C_6H_6	120	10	
Wax,	$C_{46}H_{92}O_2$*	60	10	3·5
Stearine,	$C_{57}H_{110}O_6$	62·1	10	8·7
Oleine,	$C_{57}H_{104}O_6$	65·8	10	9·2
Alcohol,	C_2H_6O	40	10	27
Wood naphtha,	CH_4O	30	10	40

It may be stated generally that when the number of atoms of carbon is less than half that of hydrogen, the flame will be free from smoke, as in the case of marsh-gas. When there are half as many atoms of carbon as of hydrogen, as in olefiant gas, the flame is very liable to smoke, unless managed with great judgment. Those hydro-carbons which contain, like turpentine and benzole, a larger proportion of carbon than this, always burn with much smoke, and require special contrivance to render them applicable for illuminating purposes. Thus, camphine (turpentine) must be burnt in lamps with tall narrow chimneys of peculiar construction to

* This is the composition of myricine, which forms the greater part of bees' wax.

afford a strong current of air. Benzole (coal-naphtha) vapour must be mixed with air if it is required to burn with a smokeless flame.

If a piece of cotton wool, moistened with benzole, be placed in a flask provided with two tubes (fig. 119), it will be found, on gently warming the flask by dipping it into hot water, and blowing through one of the tubes, that the mixture of benzole vapour and air issuing from the other tube will burn with a smokeless bright flame.

If coal-gas, which is essentially a mixture of hydrogen, marsh-gas, and olefiant gas, and generally contains rather too much hydrogen in proportion to its carbon, be enriched with carbon by passing over benzole (light coal naphtha), it burns with a far more luminous flame (*naphthalised gas*).

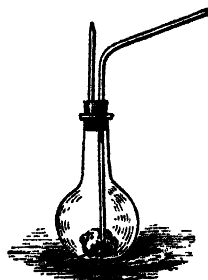


Fig. 119.

When the fuel contains oxygen, the carbon may exist in larger proportion to the hydrogen without giving rise to the production of smoke, since this oxygen will dispose of a portion of the carbon during the combustion. Thus, wax is much less liable to smoke than olefiant gas, although containing the same proportions of carbon and hydrogen, whilst stearine (the chief part of tallow) and oleine (forming the bulk of oils) may be burnt in ordinary candles and lamps, although still richer in carbon, because they contain more oxygen also.

Alcohol yields a flame of no illuminating value, although it contains more carbon in proportion to its hydrogen than is present in marsh-gas, because its oxygen helps to consume the carbon during the combustion, and prevents it from separating in the incandescent state. By adding about one-tenth of its bulk of benzole or turpentine, however, alcohol may be made to burn with a brilliant flame.

76. *The blowpipe flame.*—The principles already laid down will render the structure of the blowpipe flame easily intelligible. It must be remembered that in using the blowpipe, the stream of air is not propelled from the lungs of the operator (where a great part of its oxygen would have been consumed), but simply from the mouth, by the action of the muscles of the cheeks. The first apparent effect upon the flame is entirely to destroy its luminosity, the free supply of air effecting the immediate combustion of the carbon. The size of the flame, moreover, is much diminished, and the combustion being concentrated into a smaller space, the temperature must be much higher at any given point of the flame. In structure, the blowpipe flame is similar to the ordinary flame, consisting of three distinct cones, the innermost of which (A, fig. 120) is filled with the cool mixture of air and combustible gas. The second cone, especially at its point (R), is termed the *reducing* flame, for the supply of oxygen at that part is not sufficient to convert the carbon into carbonic acid, but leaves it as carbonic oxide, which speedily reduces almost all metallic oxides placed in that part of the flame to the metallic state. The outermost cone (O) is called the *oxidising* flame, for there the supply of oxygen from the sur-

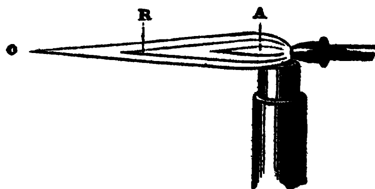


Fig. 120.—Blowpipe Flame.

rounding air is unlimited, and any substance prone to combine with oxygen at a high temperature is oxidised when exposed to the action of that portion of the flame; the hottest point of the blowpipe flame, where neither fuel nor oxygen is in excess, appears to be a very little in advance of the extremity of the second (reducing) cone. The difference in the operation of the two flames is readily shown by placing a little red lead (oxide of lead) in a shallow cavity scooped upon the surface of a piece of charcoal (fig. 121), and directing the flames upon it in succession; the inner flame will reduce a globule of metallic lead, which may be reconverted into oxide by exposing it to the outer



Fig. 121.—Reduction of metals on charcoal.

flame.* The immense service rendered by this instrument to the chemist and mineralogist is well known.

By forcing a stream of oxygen through a flame from a gas-holder or bag, an intensely hot blowpipe flame is obtained, in which pipe-clay and platinum may be melted, and iron burns with great brilliancy (see fig. 56).

Fletcher's *hot-blast blowpipe* (fig. 122), produces a much higher temperature than the ordinary blowpipe. Coal-gas is supplied through the tube *g*, and is kindled at the Bunsen burners *b h* and at the orifice *f*, the supply to the former being regulated by the stopcock *c*, and to the latter by the stopcock *d*. The flames of the Bunsen burners heat the spiral copper tube *e* to redness, so that the air blown in through the flexible tube *a* is strongly heated before being projected into the flame through a blowpipe jet at *f*. Thin platinum wires melt easily in this flame, and thin iron wires burn away rapidly.

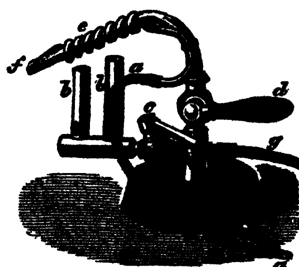


Fig. 122.—Hot-blast blowpipe.

77. *Determination of the composition of gases containing carbon and hydrogen.*—In order to ascertain the proportions of carbon and hydrogen present in a gas, a measured volume of the gas is mixed with an excess of oxygen, the volume of the mixture carefully noted, and explosion determined by passing the electric spark; the gas remaining after the explosion is measured and shaken with potash, which absorbs the carbonic acid, from the volume of which the proportion of carbon may be calculated. For example,

	0·4	cubic inch of	marsh-gas, mixed with
	1·0	„	oxygen, and exploded, left
	0·6	„	gas; shaken with potash
it left	0·2	„	oxygen.

* By directing the reducing flame upon the metallic oxide in the cavity, and allowing the oxidising flame to sweep over the surface of the charcoal, as shown in the figure, a yellow *incrustation* of oxide of lead is formed upon the surface of the charcoal, which affords additional evidence of the nature of the metal.

Showing that 0·4 cubic inch of carbonic acid had been produced. This quantity of carbonic acid would contain 0·4 cubic inch of oxygen. Deducting this last from the total amount of oxygen consumed (0·8 cubic inch), we have 0·4 cubic inch for the volume of oxygen consumed by the hydrogen. Now, 0·4 cubic inch of oxygen would combine with 0·8 cubic inch of hydrogen, which represents therefore the amount of hydrogen in the marsh-gas employed. It has thus been ascertained that the marsh-gas contains twice its volume of hydrogen.

Sp. Gr. (to H) or weight of 1 volume of marsh-gas, . .	= 8
Weight of 2 volumes (one molecule), . .	= 16
2 volumes of marsh-gas contain 4 volumes H, weighing .	4
2 volumes of marsh-gas contain x volume C, weighing .	12

For the purpose of illustration, the analysis of marsh-gas may be effected in a Ure's eudiometer (fig. 123), but a considerable excess of oxygen should be added to moderate the explosion. The eudiometer having been filled with water, 0·1 cubic inch of marsh-gas is introduced into it, as described at p. 34, and having been transferred to the closed limb and accurately measured after equalising the level of the water, the open limb is again filled up with water, the eudiometer inverted in the trough, and 1·2 cubic inch of oxygen added; this is also transferred to the closed limb and carefully measured. The electric spark is passed through the mixture (see p. 34), the open limb being closed by the thumb. The level of the water in both limbs is then equalised, and the volume of gas measured. The open limb is filled up with a strong solution of potash, and closed by the thumb, so that the gas may be transferred from the closed to the open limb and back, until its volume is no longer diminished by the absorption of carbonic acid. The volume of residual oxygen having been measured, the calculation is effected as above described.



Fig. 123.
Siphon eudiometer.

The results are more exact when the eudiometer is filled with mercury instead of water.

Coal-Gas.

78. The manufacture of coal-gas is one of the most important applications of the principle of destructive distillation, and affords an excellent example of the tendency of this process to develope new arrangements of the elements of a compound body. The action of heat upon coal, in a vessel from which air is excluded, gives rise to the production of a very large number of compounds containing some two or more of the five elements of the coal, in different proportions, or in different forms of arrangement. Although no clue has yet been obtained to indicate the true arrangement of these elements in the original coal (or, as it is termed, the *constitution* of the coal), it is certain that these various compounds do not exist in it before the application of heat, but are really the results of its action, that they are indeed *products* and not *educts*.

The most important forms assumed by the carbon and hydrogen when coal is strongly heated, are,—

Gases		Liquids		Solids	
Hydrogen,		Bensole,	C_6H_6	Naphthaline,	$C_{10}H_8$
Marsh-gas,	CH_4	Toluole,	C_7H_8	Anthracene,	$C_{14}H_{10}$
Olefiant gas,	C_2H_4			Paraffine,	C_nH_{2n+2}
Acetylene,	C_2H_2			*Coke*, .	C
Oil-gas,	C_4H_8				

The nitrogen of the coal reappears in the forms of—

Gases	Nitrogen.		
	Ammonia,	NH_3	Alkaline.
Liquids	Aniline,	C_6H_7N	Alkaline.
	Quinoline,	C_9H_7N	Alkaline.
	Hydrocyanic acid,	CHN	

The oxygen contributes to the production of—

Gases	Carbonic oxide,	CO	Liquids	Water,	H_2O
	Carbonic acid,	CO_2		Acetic acid,	$C_2H_4O_2$
				Carbolic acid,	C_6H_6O

Sulphur is found among the products as,

Sulphuretted hydrogen gas,	H_2S	Liquid (very volatile).	Bisulphide of carbon, CS_2

The illuminating gas obtained from coal consists essentially of free hydrogen, marsh-gas, olefiant gas, and carbonic oxide, with small quantities of acetylene, benzole vapour, and some other substances.

A fair general idea of its composition is given by the following table :—

Gas from Cannel Coal.

Hydrogen,	45·847	volumes.
Marsh-gas,	40·948	,,
Carbonic oxide,	4·167	,,
Olefiant gas,	5·504	,,
Carbonic acid,	1·950	,,
Nitrogen,	1·445	,,
Oxygen,	0·139	,,
	100·0	

The only constituents which contribute directly to the illuminating value of the gas are the marsh gas, olefiant gas, and similar hydrocarbons (acetylene, and benzole vapour).

The most objectionable constituent is the sulphur present as sulphuretted hydrogen and bisulphide of carbon, for this is converted by combustion into sulphuric acid, which seriously injures pictures, furniture, &c. The object of the manufacturer of coal-gas is to remove, as far as possible, everything from it, except the constituents mentioned as essential, and at the same time to obtain as large a volume of gas from a given weight of coal as is consistent with a good illuminating value.

The mode of purifying the gas, and the general arrangements for its manufacture, will be described in a later part of the work.

Fig. 124.—Destructive distillation of coal.

The destructive distillation of coal may be exhibited with the arrangement represented in fig. 124. The solid and liquid products (tar, ammoniacal liquor, &c.) are

condensed in the globular receiver (A). The first bent tube contains, in one limb (B), a piece of red litmus paper to detect ammonia; and in the other (C) a piece of paper impregnated with acetate of lead, which will be blackened by the sulphuretted hydrogen. The second bent tube (D) contains enough lime-water to fill the bend, which will be rendered milky by the carbonic acid. The gas is collected over water, in the jar E, which is furnished with a jet from which the gas may be burnt when forced out by depressing the jar in water.

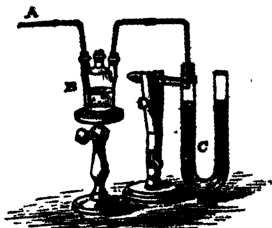


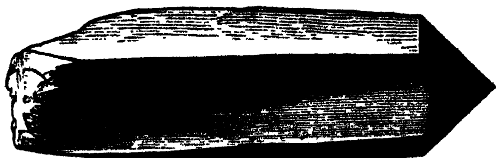
Fig. 125.

The presence of acetylene in coal-gas may be shown by passing the gas from the supply-pipe (A, fig. 125), first through a bottle (B) containing a little ammonia, then through a bent tube (C), with enough water to fill the bend, and a piece of bright sheet copper immersed in the water in each limb. After a short time the bright red flakes of the acetylide of copper will be seen in the water.

SILICON.

79. In many of its chemical relations to other bodies this element will be found to bear a great resemblance to carbon; but whilst carbon is remarkable for the great variety of compound forms in which it is met with in nature, silicon is always found in combination with oxygen, as silicic acid, or silica (SiO_2), either alone or united with various metallic oxides, with which it forms *silicates*.

Silica $SiO_2 = 60$ parts by weight.—The purest natural variety of silica is the transparent and colourless variety of quartz known as *rock crystal*, the most widely diffused ornament of the mineral world, often seen crystallised in beautiful six-sided prisms, terminated by six-sided pyramids (fig. 126), which are always easily distinguished by their great hardness, scratching glass almost as readily as the diamond. Coloured of a delicate purple, probably by a little organic matter, these crystals are known as *amethyst*; and when of a brown colour, as *Cairngorm stones* or *Scotch pebbles*. Losing its transparency and crystalline structure, we meet with silica in the form of *chalcedony* and of *carnelian*, usually coloured, in the latter, with oxide of iron.


Fig. 126.—Crystal of quartz.

Hardly any substance has so great a share in the lapidary's art as silica, for in addition to the above instances of its value for ornamental purposes we find it constituting *agate*, *cat's eye*, *onyx*, so much prized for cameos, *opal*, and some other precious stones. In opal the silica is combined with water.

Sand, of which the whiter varieties are nearly pure silica, appears to have been formed by the disintegration of siliceous rocks, and has generally a yellow or brown colour, due to the presence of oxide of iron.

The resistance offered by silica to all impressions has become proverbial in the case of *flint*, which consists essentially of that substance coloured with some impurity. Flints are generally found in compact masses, distributed in regular beds throughout the chalk formation; their hardness,

which even exceeds that of quartz, formerly rendered them useful for striking sparks with steel, by detaching small particles of the metal, which are so heated by the percussion as to continue to burn (see p. 27) in the air, and to inflame tinder or gunpowder upon which they are allowed to fall.

The part taken by silica in natural operations appears to be chiefly a mechanical one, for which its stability under ordinary influences peculiarly fits it, for it is found to constitute the great bulk of the soil which serves as a support and food-reservoir of land-plants, and enters largely into the composition of the greater number of rocks.

But that this substance is not altogether excluded from any share in life is shown by its presence in the shining outer sheath of the stems of the grasses and cereals, particularly in the hard external coating of the Dutch rush used for polishing; and this alone would lead to the inference that silica could not be absolutely insoluble, since the capillary vessels of plants are known to be capable of absorbing only such substances as are in a state of solution. Many natural waters also present us with silica in a dissolved state, and often in considerable quantity, as, for example, in the Geysers of Iceland, which deposit a coating of silica upon the earth around their borders.

Pure water, however, has no solvent action upon the natural varieties of silica. The action of an akali is required to bring it into a soluble form.

To effect this upon the small scale, a few crystals of common washing-soda (carbonate of soda) may be powdered and dried; a little of the dried powder is placed upon a piece of platinum foil slightly bent up (fig. 127),



Fig. 127.—Fusion on platinum foil.

and is fused by directing the flame of a blowpipe upon the under side of the foil. As soon as the carbonate of soda is perfectly liquefied, a small quantity of very finely powdered white sand is thrown into it, when brisk effervescence will be observed, and the particles of sand will dissolve; fresh portions of sand may now be added as long as they produce effervescence, which is due to the escape of the carbonic acid, and since, in general, one acid can only be displaced by another, it is but reasonable to infer that the sand really possesses acid properties, and hence the fitness of its chemical name, *silicic acid.*

The piece of platinum foil with the melted mass upon it may now be placed in a little warm water, and allowed to soak for some time, when it will gradually dissolve, forming a solution of *silicate of soda.* This solution will be found decidedly alkaline to test-papers; for silicic acid, like carbonic, is too feeble an acid to neutralise entirely the alkaline properties of the soda.

If a portion of the solution of silicate of soda in water be poured into a test-tube, and two or three drops of hydrochloric acid added to it, with

occasional agitation, effervescence will be produced by the expulsion of any carbonic acid still remaining, and the solution will be converted into a gelatinous mass by the separation of hydrated silicic acid. But if another portion of the solution of silicate of soda be poured into an excess of dilute hydrochloric acid (*i.e.*, into enough to render the solution distinctly acid), the silicic acid will remain dissolved in the water, together with the chloride of sodium formed by the action of the hydrochloric acid upon the soda.

In order to separate the chloride of sodium from the silicic acid, the process of *dialysis** must be resorted to.

Dialysis is the separation of dissolved substances from each other by taking advantage of the different rates at which they pass through moist diaphragms or *septa.*

If the mixed solution of chloride of sodium and silicic acid were poured upon an ordinary paper filter, it would pass through without alteration; but if parchment paper be employed, which is not pervious to water, although readily moistened by it, none of the liquid will pass through. If the cone of parchment paper be supported upon a vessel filled with distilled water (fig. 128), so that the water may be in contact with the outer surface of the cone, the hydrochloric acid and the chloride of sodium will pass through the substance of the parchment paper, and the water charged with them may be seen descending in dense streams from the outside of the cone. After a few hours, especially if the water be changed occasionally, the whole of the hydrochloric acid and chloride of sodium will have passed through, and a pure solution of silicic acid in water will remain in the cone.



Fig. 128.

This solution of silicic acid is very feebly acid to blue litmus paper, and not perceptibly sour to the taste. It has a great tendency to set into a jelly in consequence of the sudden separation of hydrated silicic acid. If it be slowly evaporated in a dish, it soon solidifies; but, by conducting the evaporation in a flask, so as to prevent any drying of the silicic acid at the edges of the liquid, it may be concentrated until it contains 14 per cent. of silicic acid. When this solution is kept, even in a stoppered or corked bottle, it sets into a transparent gelatinous mass, which gradually shrinks and separates from the water. When evaporated, *in vacuo,* over sulphuric acid, it gives a transparent lustrous glass which is composed of 22 per cent. of water and 78 per cent. of silicic acid ($H_2O.SiO_2$).

This hydrate of silica cannot be redissolved in water, and is only soluble to a slight extent in hydrochloric acid. If it be heated to expel the water, the anhydrous silicic acid which remains is insoluble both in water and in hydrochloric acid, but is dissolved when boiled with solution of potash or soda, or their carbonates.

Silicic acid in the naturally crystallised form, as rock crystal and quartz, is insoluble in boiling solutions of the alkalies, and in all acids except hydrofluoric; but amorphous silica (such as that found at Farnham) is readily dissolved by boiling alkalies. These represent, in fact, two distinct modifications of silica. A transparent piece of rock crystal may be heated to bright redness without change, but if it be powdered previously to being heated, its specific gravity is diminished from 2·6 to 2·4, and it

* From διαλύω, to part asunder.

becomes soluble in boiling alkalies, having been converted into the amorphous modification.

Crystals of quartz have been obtained artificially by the prolonged action of water upon glass at a high temperature under pressure. When fused with the oxyhydrogen blowpipe, silica does not crystallise, being thus converted into the amorphous variety of sp. gr. 2·3.

To prepare the amorphous modification of silica artificially, white sand in very fine powder may be fused, in a platinum crucible, with six times its weight of a mixture of equal weights of carbonate of potash and carbonate of soda, the mixture being more easily fusible than either of the carbonates separately. The crucible may be heated over a gas-burner supplied with a mixture of gas and air, or may be placed in a little calcined magnesia contained in a fire-clay crucible, which may be covered up and introduced into a good fire. The platinum crucible is never heated in direct contact with fuel, since the metal would become brittle by combining with carbon, silicon, and sulphur derived from the fuel. The magnesia is used to protect the platinum from contact with the clay crucible. When the action of the silicic acid upon the alkaline carbonates is completed, which will be indicated by the cessation of the effervescence, the platinum crucible is allowed to cool, placed in an evaporating dish, and soaked for a night in water, when the mass should be entirely dissolved. Hydrochloric acid is then added to the solution, with occasional stirring, until it is distinctly acid to litmus paper. On evaporating the solution, it will, at a certain point, solidify to a gelatinous mass of hydrated silicic acid, which would be spirted out of the dish if evaporation over the flame were continued. To prevent this, the dish is placed over an empty iron saucepan (fig. 129), so that the heat from the flame may be equally distributed over the bottom of the dish. When the mass is quite dry, the dish is allowed to cool, and some water is poured into it, which dissolves the chlorides of potassium and sodium (formed by the action of the hydrochloric acid upon the silicates of potash and soda), and leaves the silicic acid in white flakes. These may be collected upon a filter (fig. 130), and washed several times with distilled water. The filter is then carefully spread out upon a hot iron plate, or upon a hot brick, and allowed to dry, when the silicic acid is left as a dazzling white powder, which must be strongly heated in a porcelain or platinum crucible to expel the last traces of water. It is remarkable for its extreme lightness, especially when heated, the slightest current of air easily blowing it away.

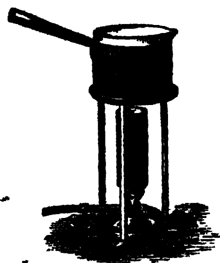


Fig. 129.



Fig. 130.—Washing a precipitate.

80. For effecting such fusions as that just described, an air-gas blow-pipe (A, fig. 131) supplied with air from a double action bellows (B), worked by a treadle (C), will be found most convenient. Where gas is not at hand, the fusion may be effected in a small furnace (fig. 132), surmounted with a conical chimney, and fed with charcoal.

81. *Silicates.*—The acid properties of silicic acid are so feeble that it is a matter of great difficulty to determine the proportion of any base which is required to unite with it in order to form a chemically neutral salt. Like carbonic acid, it does not destroy the action of the alkalies upon test-papers, and we are, therefore, deprived of this method of

ascertaining the proportion of alkali which neutralises it in a chemical sense. In attempting to ascertain the quantity of alkali with which it combines from that of the carbonic acid which it expels when heated with an alkaline carbonate, it is found that the proportion of carbonic acid expelled varies considerably, according to the temperature and the proportion of alkaline carbonate employed, probably because the attractions of silicic and carbonic acids for the alkaline bases are pretty evenly balanced.

By heating silicic acid with hydrate of soda ($Na_2O.H_2O$), it is found that 60 parts of silicic acid expel 36 parts of water, however much hydrate of soda is employed, and the same proportion of water is expelled from hydrate of baryta ($BaO.H_2O$) when heated with silicic acid.

The formula SiO_2 represents 60 parts by weight of silicic acid, and 36 parts represent two molecules of water which were combined in the hydrates with soda and baryta respectively. Hence it would appear that one molecule of silicic acid is disposed to combine with two molecules of an alkali, and since it is found that several of the crystallised mineral silicates contain a quantity of base equivalent to two molecules of an alkali combined with one molecule of silicic acid, it is usual to represent it as a *tetrabasic* acid, that is, an acid requiring two molecules of an alkali (containing *four* atoms of metal) to form a chemically neutral salt.

The circumstance that silicic acid is not capable of being converted into vapour at a high temperature, enables it to expel from their combinations with bases many other acids which, at ordinary temperatures, are able to displace silicic acid. Thus, sulphuric acid has a far more powerful attraction for bases than silicic acid, at the ordinary temperature, but when a mixture of silicic acid with a sulphate is strongly heated, the tendency of the sulphuric acid to assume the vaporous state at this temperature determines the decomposition of the sulphate and the formation of a silicate.

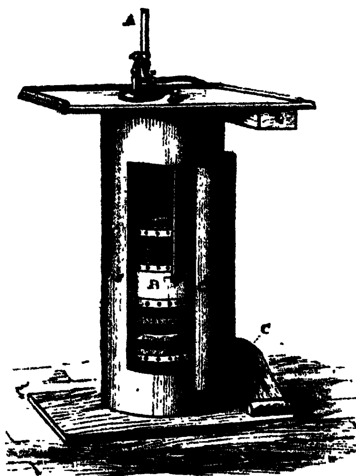


Fig. 131.—Air-gas blowpipe table.

The silicates form by far the greatest number of minerals. The different varieties of clay consist of silicate of alumina; feldspar is a silicate of alumina and potash; meerschaum is a silicate of magnesia.

The different kinds of glass are composed of silicates of potash, soda, lime, oxide of lead, &c.

None but the silicates of the alkalies are soluble in water.

82. *Silicon* or *Silicium* (Si = 28 parts by weight).—From the remarkably unchangeable character of silica, it is not surprising that it was long regarded as an elementary substance. In 1813, however, Davy succeeded in decomposing it by the action of potassium, and in obtaining an impure specimen of silicon. It has since been produced, far more easily, by converting the silicic acid into silico-fluoride of potassium ($2KF.SiF_4$), and decomposing this at a high temperature with potassium or sodium, which

combines with the fluorine to form a salt capable of being dissolved out by water, leaving the silicon in the form of a brown powder (*amorphous silicon*) which resists the action of all acids, except hydrofluoric, which it decomposes, forming fluoride of silicon and evolving hydrogen ($Si + 4HF = SiF_4 + H_4$). It is also dissolved by solution of hydrate of potash, with evolution of hydrogen, and formation of silicate of potash. It burns brilliantly when heated in oxygen, but not completely, for it becomes coated with silica which is fused by the intense heat of the combustion. When heated with the blowpipe on platinum foil, it eats a hole through the metal, with which it forms the fusible silicide of platinum.

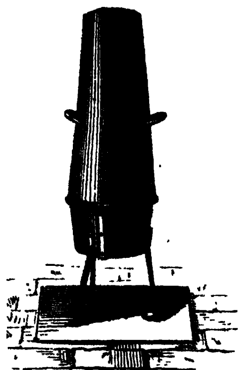


Fig. 132.—Charcoal furnace.

If silico-fluoride of potassium be fused with aluminum, a portion of the latter combines with the fluorine, and the remainder combines with the silicon, forming a silicide of aluminum. By boiling this with hydrochloric and hydrofluoric acids in succession, the aluminum is extracted, and crystalline scales of silicon, with a metallic lustre resembling black lead, are left (*graphitoid silicon*). In this form the silicon has a specific gravity of about 2·5, and refuses to burn in oxygen, or to dissolve in hydrofluoric acid. A mixture of nitric and hydrofluoric acids, however, is capable of dissolving it. Like graphite, this variety of silicon conducts electricity, though amorphous silicon is a non-conductor. The amorphous silicon becomes converted into this incombustible and insoluble form under the action of intense heat. It is worthy of remark that the combustibility of amorphous carbon (charcoal) is also very much diminished by exposure to a high temperature.

Unlike carbon, however, silicon is capable of being fused at a temperature somewhat above the melting point of cast iron; on cooling it forms a brilliant metallic-looking mass, which may be obtained, by certain processes, crystallised in octahedra so hard as to scratch glass like a diamond.

In their chemical relations to other substances there is much resemblance between silicon and carbon. They both form feeble acids with oxygen, which correspond in composition. Silicon, however, is capable of displacing carbon from carbonic acid, for if carbonate of potash be fused with silicon, the latter is dissolved, forming silicate of potash, and carbon is separated. Silicon also resembles carbon in its disposition to unite with certain metals to form compounds which still retain their metallic appearance. Thus silicon is found together with carbon in cast iron, and it unites directly with aluminum, zinc, and platinum, to form compounds resembling metallic alloys. Nitrogen enters into direct union with silicon at a high temperature, though it refuses to unite with carbon except in the presence of alkalies. In their relation to hydrogen, these two elements are widely different, for silicon is only known to form one compound with hydrogen, and that of a very unstable character.

The *hydride of silicon* has been found to have a composition corresponding with the formula SiH_4. It derives its interest chiefly from the property of taking fire spontaneously in contact with the air, in which it

burns with a brilliant white flame, giving off clouds of silica, and depositing a brown film of silicon upon a cold surface.

Hydride of silicon is prepared by decomposing silicide of magnesium with dilute hydrochloric acid. The silicide of magnesium is obtained by fusing chloride of magnesium ($MgCl_2$) with silico-fluoride of sodium ($2NaF . SiF_4$), and metallic sodium, when the latter combines with the chlorine and fluorine, leaving the magnesium free to unite with the silicon.

The chloride of magnesium may be prepared by dissolving ordinary carbonate of magnesia in hydrochloric acid, adding three parts of chloride of ammonium for each part of carbonate of magnesia, evaporating to dryness in a porcelain dish, fusing the residue, and pouring it out on to a clean stone. Being very deliquescent, it must be kept in a well-closed bottle.

Silico-fluoride of sodium is made by neutralising hydro-fluosilicic acid with carbonate of soda, and evaporating to dryness.

To increase the fusibility of the mixture, some fused common salt will be required. Dried salt may be melted in a fire-clay crucible, at a bright red heat, and poured out upon a clean dry stone.

Forty parts of the chloride of magnesium, 35 of silico-fluoride of sodium, 10 of fused chloride of sodium, and 20 of sodium in slices, are rapidly weighed, shaken together in a dry bottle, and thrown into a red-hot clay crucible, which is then covered and heated as long as the yellow flame of sodium vapour is perceptible. After cooling, the crucible is broken, when a dark-coloured layer of silicide of magnesium will be found beneath a white layer of chloride and fluoride of sodium. The silicide of magnesium must be rapidly detached, and preserved in a well-stopped bottle.

The silicide of magnesium is coarsely powdered, and introduced into a Woulfe's bottle (fig. 133) provided with a funnel tube, and a short wide tube for delivering the gas. The bottle is filled up with water (previously boiled to expel air, and allowed to cool), and placed in the pneumatic trough (containing boiled water), so that both bottle and tubes may remain filled with water. A gas-jar, filled with boiled water, having been placed over the delivery-tube, some strong hydrochloric acid is added through the funnel, great care being taken that no air shall enter. The hydride of silicon is at once evolved, and must be allowed to stand over water for some little time, to allow the froth, caused by a slight separation of silica, to subside. The gas may then be transferred to a capped jar, with a stop-cock, from which it may be allowed to pass into the air for the examination of its flame.

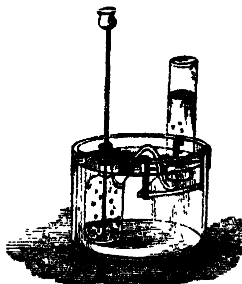


Fig. 133.

When cast iron, containing silicon, is boiled with hydrochloric acid until the whole of the iron is dissolved, a grey frothy residue is left. If this be collected on a filter, well washed and dried, it is found to consist of black scales of graphite, mixed with a very light white powder. On boiling it with potash, hydrogen is evolved, and the white powder dissolves, forming a solution containing silicate of potash. This white powder appears to be identical with a substance obtained by other processes, and called *leucone*,* which is believed to have the composition $Si_3H_4O_5$, and has been regarded as a hydride of protoxide of silicon, $3SiO . 2H_2O$. Its action upon solution of potash would be explained by the equation



$$Si_3H_4O_5 + 12KHO = 3(2K_2O . SiO_2) + H_6 + 5H_2O.$$

Leucone is slowly converted into silicic acid, even by the action of water, hydrogen being disengaged.

Another compound, containing silicon, hydrogen, and oxygen, has been named *silicone*. It is a yellow substance, the general characters of which resemble those of the compound last described. When exposed, under water, to the action of sunlight, hydrogen is evolved, and the yellow body becomes converted into leucone.

The *atomic weight* of silicon is generally represented by the number

* Λευκὸς, white.

28, though here, as in the case of carbon, theoretical considerations are relied upon, since the specific gravity of vapour of silicon cannot be ascertained by experiment, and no assistance is afforded by the specific heat.

BORON.

83. Closely allied to silicon is another element, boron, which has at present never been found in animal or vegetable bodies, but appears to be entirely confined to the mineral kingdom.

Boracic acid ($B_2O_3 = 69 \cdot 8$ parts by weight).—A saline substance called *borax* ($Na_2O.2B_2O_3$, 10Aq.), has long been used in medicine, in working metals, and in making imitations of precious stones; this substance was originally imported from India and Thibet, where it was obtained in crystals from the waters of certain lakes, and came into this country under the native designation of *tincal*, consisting of impure borax, surrounded with a peculiar soapy substance, which the refiner of borax makes it his business to remove.

In 1702, in the course of one of those tentative experiments to which, though empirical in their nature, scientific chemistry is now so deeply indebted, Homberg happened to distil a mixture of borax and green vitriol (sulphate of iron), when he obtained a new substance in pearly plates, which was found useful in medicine, and received the name of *sedative salt*. A quarter of a century later, Lemery found that this substance might be separated from borax by employing sulphuric acid instead of sulphate of iron; but another quarter of a century elapsed before it was shown that in borax these pearly crystalline scales were combined with soda, and were possessed of acid properties which entitle them to receive the name *boracic acid*.

Much more recently this acid has been obtained in a free state from natural sources, and is now largely imported into this country from the volcanic districts in the north of Italy, where it issues from the earth in

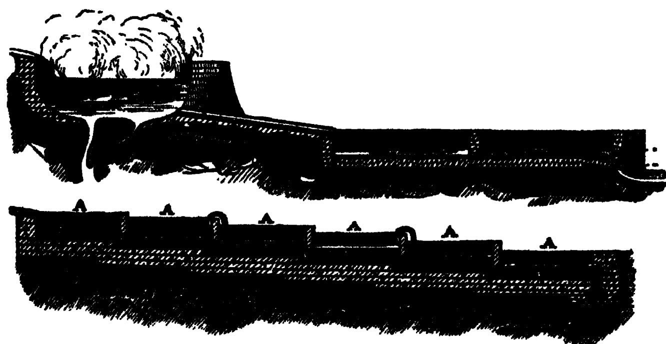


Fig. 134.—Boracic lagune and evaporating pans.

the form of vapour, accompanied by violent jets of steam, which are known in the neighbourhood as *soffioni*. It would appear easy enough, by adopting arrangements for the condensation of this steam, to obtain the boracic acid which accompanies it, but it is found necessary to cause the steam to deposit its boracic acid by passing it through water, for which purpose basins of brickwork (*lagunes*, fig. 134) are built up around

the soffioni, and are kept filled with water from the neighbouring springs or brooks; this water is allowed to flow successively into the different lagunes, which are built upon a declivity for that purpose, and it thus becomes impregnated with about 1 per cent. of boracic acid. The necessity for expelling a large proportion of this water, in order to obtain the boracic acid in crystals, formed for a long time a great obstacle to the success of this branch of industry in a country where fuel is very expensive. In 1817, however, Larderello conceived the project of evaporating this water by the steam-heat afforded by the soffioni themselves, and several hundred tons of boracic acid are now annually produced in this manner. The evaporation is conducted in shallow leaden evaporating pans (A, fig. 134), under which the steam from the soffioni is conducted through the flues (F) constructed for that purpose. As the demand for boracic acid increased on account of the immense consumption of borax in the porcelain manufacture, the experiment was made, with success, of boring into the volcanic strata, and thus producing artificial soffioni, yielding boracic acid.

The crystals of boracic acid, as imported from these sources, contain salts of ammonia and other impurities. They dissolve in about three times their weight of boiling water, and crystallise out on cooling, since they require 26 parts of cold water to dissolve them. These crystals are represented by the formula $3H_2O.B_2O_3$. If they are sharply heated in a retort, they partly distil over unchanged, together with the water derived from the decomposition of another part; but if they be heated to 212° F. only, they effloresce, and become converted into $H_2O.B_2O_3$. When this is further heated, the whole of the water passes off, carrying with it a little boracic acid, and the acid fuses to a glass, which remains perfectly transparent on cooling (*vitreous boracic acid*). This anhydrous boracic acid is slowly volatilised by the continued action of a very high temperature. It dissolves very slowly in water.

A characteristic property of boracic acid is that of imparting a green colour to flames. Its presence may thus be detected in the steam issuing from a boiling solution of boracic acid in water, for if a spirit-lamp flame, or a piece of burning paper, be held in the steam, the flame will acquire a green tint, especially at the edges.

The colour is more distinctly seen when the crystallised boracic acid is heated on platinum foil in a spirit-flame or an air-gas flame; and still better when the crystals are dissolved in boiling alcohol, and the solution burnt on a plate. The presence of boracic acid in borax may be ascertained by mixing the solution of borax with strong sulphuric acid to liberate the boracic acid, and adding enough alcohol to make the mixture burn. Another peculiar property of boracic acid is its action upon turmeric. If a piece of turmeric paper be dipped in solution of boracic acid, and dried at a gentle heat, it assumes a fine brown-red colour, which is changed to green or blue by potash or its carbonate. In applying this test to borax, the solution is slightly acidified with hydrochloric acid, to set free the boracic acid, before dipping the paper.

Borates.—Boracic acid, like silicic, must be classed among the feeble acids. It colours litmus violet only, like carbonic acid, and does not neutralise the action of the alkalies upon test-papers. At high temperatures fused boracic acid dissolves the metallic oxides to form transparent glassy borates, which have, in many cases, very brilliant colours, and upon this property depend the chief uses of boracic acid in the arts.

Unlike the silicates, the borates are comparatively rare in the mineral world. No very familiar mineral substance contains boracic acid. A

double borate of soda and lime, called *boro-natrocalcite* ($Na_2O.2B_2O_3$, $2(CaO.2B_2O_3)$, $18H_2O$), is imported from Peru for the manufacture of borax; and the mineral known as *boracite* is a borate of magnesia.

In determining the proportion of base which boracic acid requires to form with it a chemically neutral salt, the same difficulties are met with as in the case of silicic acid (p. 112); but since it is found that 69·8 parts of boracic acid (the weight represented by B_2O_3) displace 54 parts of water (three molecules) from hydrate of soda and from hydrate of baryta, both employed in excess, it would appear that the boracic acid requires three molecules of an alkali fully to satisfy its acid character.

84. *Boron.*—B = 10·9 parts by weight.—It was in the year 1808 that Gay-Lussac and Thénard succeeded, by fusing anhydrous boracic acid with potassium, in extracting from it the element boron as an olive-green powder (*amorphous boron*), which has a general resemblance to silicon, but, unlike that element, may be oxidised by nitric acid. It also requires a higher temperature to fuse it than is required by silicon. The brilliant copper-coloured scales obtained by a process similar to that which furnishes the graphitoid silicon, and formerly regarded as graphitoid boron, consist really of a compound of boron with aluminum (AlB_2).

The most remarkable form of boron is the crystallised variety or *diamond of boron*, which is obtained by very strongly heating amorphous boron with aluminum, and afterwards extracting the aluminum from the mass with hydrochloric acid. These crystals are brilliant transparent octahedra, which are sometimes nearly colourless, and resemble the diamond in their power of refracting light, and in their hardness, which is so great that they will scratch rubies, and will even wear away the surface of the diamond.* This form of boron cannot be attacked by any acid, but is dissolved by fused hydrates of the alkalies. The flame of the oxyhydrogen blowpipe does not fuse it, and it only undergoes superficial conversion into boracic acid when heated to whiteness in oxygen. When heated to redness in chlorine, however, it burns, forming chloride of boron. Boron closely resembles silicon in its chemical relations to the other elements. It is not known, however, to form a compound with hydrogen, and has a greater disposition to combine with nitrogen than is manifested by silicon. It absorbs nitrogen readily when heated to redness, forming a white infusible insoluble powder, the *nitride of boron* (BN).

85. The elements carbon, boron, and silicon form a natural group, possessing many properties in common. They are all capable of existing in the amorphous, the graphitoid, and the crystalline forms; all incapable of being converted into vapour; all exhibit a want of disposition to dissolve; all form feeble acids with oxygen by direct union; and all unite with several of the metals to form compounds which resemble each other. Boron and silicon are capable of direct union with nitrogen, and so is carbon if an alkali be present. Recent researches attribute to silicon the power of occupying the place of carbon in some organic compounds, and the formulæ of leucone and silicone ($Si_4H_4O_5$ and $Si_6H_6O_4$) strongly remind us of the organic compounds of carbon with hydrogen and oxygen. In many of its physical and chemical characters, silicon is closely allied with the metals, and it will be found that tin and titanium bear a particular resemblance to it in their chemical relations.

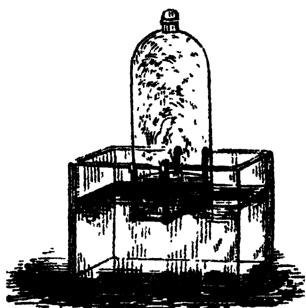
* The author has known them to cut through the bottom of the beaker-glass used in separating them from the aluminum.

NITROGEN.

N = 14 parts by weight = 1 vol. 14 grns. = 46·7 cub. in. at 60° F. and 30″ Bar.
14 grms. = 11·2 litres at 0° C. and 760 mm. Bar.

86. This element, which has already been referred to as forming four-fifths of the volume of air, is elsewhere found in nature in the forms of saltpetre or nitrate of potash (KNO_3), and Chili saltpetre or nitrate of soda ($NaNO_3$). It also occurs as ammonia (NH_3) in the atmosphere and in the gaseous emanations from volcanoes. It is contained in the greater number of animal, and in many vegetable substances, and therefore has a most important share in the chemical phenomena of life.

Nitrogen is generally obtained by burning phosphorus in a portion of air confined over water (fig. 135). The phosphorus is floated on the water in a small porcelain dish, kindled, and covered with a bell-jar. The nitrogen remains mixed with clouds of phosphoric acid (P_2O_5), which may be removed by allowing the gas to stand over water.


Fig. 135.—Preparation of nitrogen.

When nitrogen is required in larger quantity, it is more conveniently prepared by passing air from a gas-holder over metallic copper heated to redness in a tube. The negative properties of this gas, however, are so very uninteresting, and render it so useless for most chemical purposes, that it will be unnecessary to give further details respecting its preparation. The remarkable chemical inactivity of free nitrogen has been alluded to in the article on atmospheric air. It has been seen, however, to be capable of combining directly with boron and silicon, and magnesium and titanium unite with it even more readily at a high temperature. It is conspicuous among the elements for forming, with hydrogen, a powerful alkali (ammonia, NH_3), and with oxygen a powerful acid (nitric acid, N_2O_5), whilst the feeble chemical ties which hold it in combination with other elements, joined to its character of a permanent gas, render many of its compounds very unstable and explosive, as is the case with the so-called chloride and iodide of nitrogen, gun-cotton, the fulminates of silver and mercury, nitro-glycerine, &c.

The discovery of nitrogen was made by Rutherford (Professor of Botany in the University of Edinburgh) in 1772, who was led to it by the observation that respired air was still unfit to support life when all the carbonic acid had been absorbed from it by a caustic alkali. Hence the name *azote* (ἀ priv. and ζωή life) formerly bestowed upon this gas.

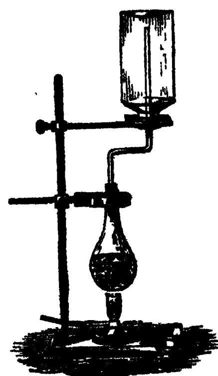
AMMONIA.

NH_3 = 17 parts by weight = 2 vols.

87. The proportion of ammonia existing in atmospheric air is so small that it is difficult to determine it with precision; it appears, however, not to exceed one-hundredth of a grain in a cubic foot. This scarcity of

ammonia in air is not to be accounted for by a scantiness in the supply, but rather by an excess in the demand; since ammonia is constantly sent forth into the air by the putrefaction of animal and vegetable substances containing nitrogen. Plants do not appear to be capable of absorbing from the atmosphere the nitrogen which it contains so abundantly in the uncombined form, but to derive their chief supply of that element from the ammonia, brought down by rain from the atmosphere, into which it is continually introduced from various sources. During the life of an animal, it restores to the air the nitrogen which formed part of its wasted organs, in part directly as ammonia in the breath and in the exhalation from the skin,* whilst another portion is separated as urea and uric acid in the urine, to be eventually converted into ammonia when the excretion undergoes putrefaction. Dead animal and vegetable matter when putrefying, restores its nitrogen to the air, chiefly in the forms of ammonia and substances closely allied to it, but partly also, it is said, in the free state.

The *liquor ammoniæ*, or solution of ammonia in water, which is so largely used in medicine and the arts, is obtained chiefly from the *ammoniacal liquor* resulting from the destructive distillation of coal for the manufacture of gas. The ammoniacal liquor of the gas-works contains ammonia in combination with carbonic and hydrosulphuric acid. As the first step towards extracting the ammonia in a pure state, the liquor is neutralised with hydrochloric acid, which combines with the ammonia, expelling the carbonic and hydrosulphuric acid gases. Since the latter has a very bad smell and is injurious to health, the neutralisation is generally effected in covered vats furnished with pipes, which convey the gases into a furnace where the hydrosulphuric acid is burnt, forming water and sulphurous acid. The solution of hydrochlorate of ammonia is evaporated to expel part of the water, and allowed to cool in wooden vessels lined with lead, where the hydrochlorate is deposited in crystals which contain a good deal of tarry matter. These crystals are moderately heated in an iron pan to deprive them of tar, and are finally purified by *sublimation*, that is, by converting them into vapour, and allowing this vapour to condense again into the solid form. For this purpose the crystals are heated in a cylindrical iron vessel covered with an iron dome lined with fire-clay. The hydrochlorate of ammonia rises in vapour below a red heat, and condenses upon the dome in the form of the fibrous cake known in commerce as *sal-ammoniac*.


Fig. 136.—Preparation of ammonia.

To obtain ammonia from this salt, an ounce of it is reduced to coarse powder, and rapidly mixed with two ounces of powdered quicklime. The mixture is gently heated in a dry Florence flask (fig. 136), and the gas, being little more than half as heavy as air (sp. gr. 0·59), may be collected in dry bottles by displacement of air, the bottles being allowed to rest upon a piece of tin plate which is perforated for the passage of the tube. To ascertain when the bottles are filled, a piece of red litmus paper may be held at some little distance above the mouth,

* Some doubt exists as to the exhalation of ammonia from the lungs and skin of man under normal conditions.

when it will at once acquire a blue colour if the ammonia escapes. The bottles should be closed with greased stoppers.

The action of the lime upon hydrochlorate of ammonia is explained by the following equation :—



$$2(NH_3.HCl) + CaO = CaCl_2 + H_2O + 2NH_3$$

Hydrochlor. amm. — Lime. — Chloride of calcium. — Ammonia.

The readiest method of obtaining gaseous ammonia for the study of its properties consists in gently heating the strongest *liquor ammoniæ* in a retort or flask provided with a bent tube for collecting the gas by displacement (fig. 137). The gas is evolved from the solution at a very low heat, and may be collected unaccompanied by steam.

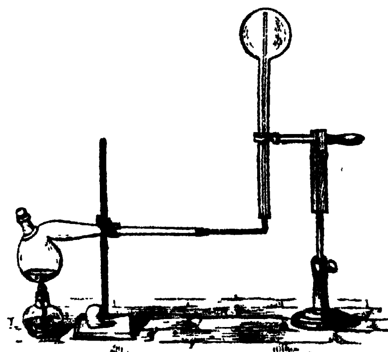


Fig. 137.

Ammonia is readily distinguished by its very characteristic smell, and its powerful alkaline action upon red litmus and turmeric papers. It is absorbed by water in greater proportion by volume than any other gas, one volume of water absorbing more than 700 volumes of ammonia at the ordinary temperature, and becoming one-and-a-half volumes of solution of ammonia of specific gravity 0·88. No chemical combination appears to take place between the water and ammonia, for the gas gradually escapes on exposing the solution to the air, and no definite compound of the two has been noticed. Moreover, the quantity of ammonia retained by the water is dependent upon the temperature and pressure, as would be expected if the ammonia were merely *dissolved* and not combined with the water. The escape of the gas from the solution is attended with great production of cold, much heat becoming latent in the conversion of the ammonia from the liquid to the gaseous state.

The rapid absorption of ammonia by water is well shown by filling a globular flask (fig. 138) with the gas, placing it with its mouth downwards in a small capsule of mercury which is placed in a large basin. If this basin be filled with water, it cannot come into contact with the ammonia until the mouth of the flask is raised out of the mercury, when the water will quickly enter and fill the flask. The water should be coloured with reddened litmus to exhibit the alkaline reaction of the ammonia.

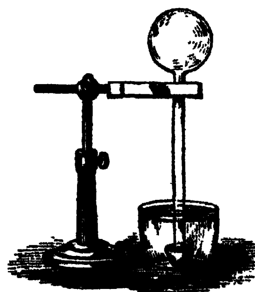
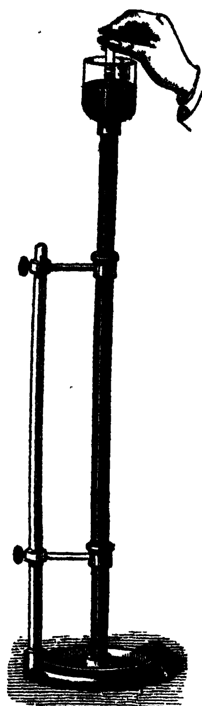


Fig. 138.

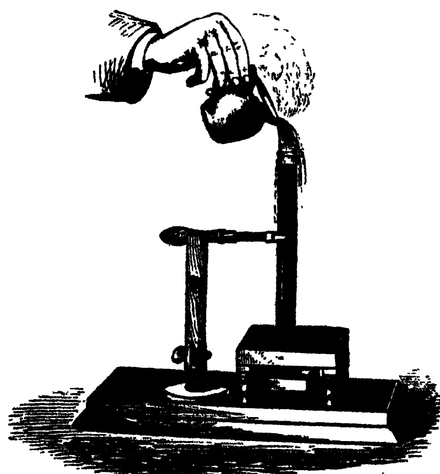
That the amount of ammonia in solution varies with the pressure, may be proved by filling a barometer tube, over 30 inches long, with mercury to within an inch of the top, filling it up with strong ammonia, closing the mouth of the tube, and inverting it with its mouth under mercury ; on removing the finger, the diminished pressure caused by the gravitation of the column of mercury in the tube will cause the solution of ammonia to boil, from the escape of a large quantity of the gas, which will rapidly depress the mercury. If the pressure be now increased by gradually depressing the tube in a tall cylinder of mercury (fig. 139), the water will again absorb the ammoniacal gas.

To exhibit the easy expulsion of the ammoniacal gas from water by heat, a moderately thick glass tube, about 12 inches long and half an inch in diameter, may be nearly filled with mercury, and then filled up with strong solution of ammonia; on closing it with the thumb and inverting it into a vessel of mercury (fig. 140) the solution will, of course, rise above the mercury to the closed end of the tube. By grasping this end of the tube in the hand, a considerable quantity of gas may be expelled, and the mercury will be depressed. If a little hot water be poured over the top of the tube, the latter will become filled with ammoniacal gas, which will be absorbed again by the water when the tube is allowed to cool, the mercury returning to fill the tube.


Fig. 139.

The solution of ammonia, which is an article of commerce, is prepared by conducting the gas into water contained in a two-necked bottle, the second neck being connected with a tube passing into another bottle containing water, in which any escaping ammonia may be condensed. The strength of the solution is inferred from its specific gravity, which is lower in proportion as the quantity of ammonia in the solution is greater.

Thus, at 57° F., a solution of sp. gr. 0·8844 contains 36 parts by weight of ammonia in 100 parts of solution; the sp. gr. 0·8976 indicates 30 per cent.; 0·9106, 25 per cent.; 0·9251, 20 per cent.; 0·9414, 15 per cent.; 0·9593, 10 per cent.; 0·979, 5 per cent. The specific gravity is ascertained by comparing the weights of equal volumes of water and of the solution at the same temperature. For this purpose, a light stoppered bottle is provided, capable of containing about two fluid ounces. This is thoroughly dried, and counterpoised in a balance by placing in the opposite pan a piece of lead, which may be cut down to the proper weight. The bottle is then filled with solution of ammonia, the temperature observed with a thermometer and recorded, the stopper inserted, and the bottle weighed. It is then well rinsed out, filled with distilled water, the temperature equalised with that of the ammonia by placing the bottle either in warm or cold water, and the weight ascertained as before. The specific gravity is obtained by dividing the weight of the solution of ammonia by that of the water. The *ammonia-meter* (fig. 141) is a convenient instrument for rapidly ascertaining the specific gravity of liquids lighter than water. It consists of a hollow glass float with a long stem, weighted with a bulb containing shot or mercury, so that when placed in distilled water it may sink to 1000° of the scale marked on the stem, this number representing the specific gravity of water. When placed in a liquid lighter than water, it must, of course, sink lower in order to displace more liquid (since solids sink until they have displaced their own weight of liquid). By trying it in liquids of known specific gravities, the mark upon the scale to which it sinks may be made to indicate the specific gravity of the liquid. The ammonia-meter


Fig. 140.

generally has a scale so divided that it indicates at once the percentage weight of ammonia. In this country the specific gravity of a liquid is always supposed to be taken at 62° F.

The common name for solution of ammonia, *spirit of hart's horn*, is derived from the circumstance that it was originally obtained for medicinal purposes by distilling shavings of that material.

When ammonia is exposed to a temperature of − 40° F. (*i.e.*, 72° below the freezing-point), or to a pressure of 6½ atmospheres at 50°, it condenses to a clear liquid, which solidifies at a temperature of − 103° F. to a white crystalline mass. The comparative ease with which it may be liquefied has led to its application in Carré's freezing apparatus (fig. 142), in which the gas generated by heating a concentrated solution of ammonia in a strong iron boiler (A) is liquefied by its own pressure in an iron receiver (B) placed in cold water. When the boiler is taken off the fire and cooled in water, the liquefied ammonia evaporates very rapidly from the receiver back into the boiler, thereby producing so much cold that a vessel of water placed in a cavity (C) in the receiver is at once congealed into ice. A refrigerator constructed upon this principle is employed in the *salt gardens* of the south of France, in order to render their crystallising operations independent of the temperature of the air.

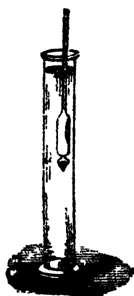


Fig. 141.

The liquefaction of ammonia is very easily effected by heating the ammoniated chloride of silver in one limb of a sealed tube, the other limb of which is cooled in a freezing mixture. A piece of stout light green glass tube (A, fig. 143), about 12

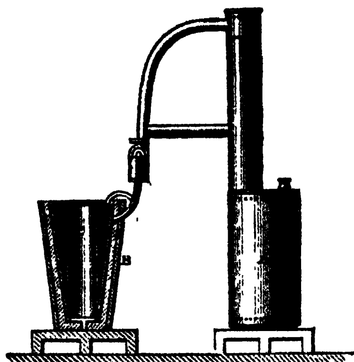


Fig. 142.—Carré's freezing apparatus.

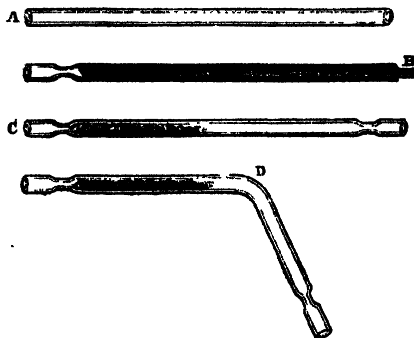


Fig. 143.

inches long and half an inch in diameter, is drawn out at about an inch from one end to a narrow neck. About 300 grains of chloride of silver (dried at 400° F.) are introduced into the tube, so as to lie loosely in it. For this purpose a gutter of stiff paper (B) should be cut so as to slide loosely in the tube, the chloride of silver placed upon it, and when it has been thrust into the tube (held horizontally) the latter should be turned upon its axis, so that the chloride of silver may fall out of the paper, which may then be withdrawn. The tube is now drawn out to a narrow neck at about an inch from the other end, as in C, and afterwards carefully bent, as in D, care being taken that none of the chloride of silver falls into the short limb of the tube, which should be about four inches long. The tube is then supported by a holder, so that the long limb may be horizontal, and is connected, by a tube and cork, with an apparatus delivering dry ammonia, prepared by heating 1000 grains of sal-ammoniac with an equal weight of quick-lime in a flask, and passing the gas, first into an empty bottle (A, fig. 144) standing in cold water, and afterwards through a bottle (B) filled with lumps of quick-lime to absorb all aqueous vapour.

The long limb of the tube must be surrounded with filtering paper, which is kept wet with cold water. The current of ammonia should be continued at a moderate



Fig. 144.

rate, until the tube and its contents no longer increase in weight, which will occupy about three hours—about 35 grains of ammonia being absorbed. The longer limb is sealed by the blowpipe flame whilst the gas is still passing, and then, as quickly as possible, the shorter limb, keeping that part of the tube which is occupied by the ammoniated chloride of silver still carefully surrounded by wet paper.

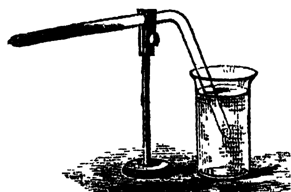


Fig. 145. –Liquefaction of ammonia.

When the shorter limb of this tube (fig. 145) is cooled in a mixture of ice and salt (or of 8 ounces of sulphate of soda and 4 measured ounces of common hydrochloric acid), whilst the longer limb is gently heated from end to end by waving a spirit flame beneath it, the ammonia evolved by the heat from the ammoniated chloride of silver, which partly fuses, will condense into a beautifully clear liquid in the cold limb. When this is withdrawn from the freezing mixture, and the tube allowed to cool, the liquid ammonia will boil and gradually disappear entirely, the gas being again absorbed by the chloride of silver, so that the tube is ready to be used again.

Ammonia is feebly combustible in atmospheric air, as may be seen by holding a taper just within the mouth of an inverted bottle of the gas, which burns with a peculiar livid flickering light around the flame, but will not continue to burn when the flame is removed. During its combustion the hydrogen is converted into water, and the nitrogen set free. In oxygen, however, ammonia burns with a continuous flame.

This is very well shown by surrounding a tube delivering a stream of ammonia (obtained by heating strong solution of ammonia in a retort) with a much wider tube open at both ends (fig. 146), through which oxygen is passed by holding a flexible tube from a gas-bag or gas-holder underneath it. On kindling the stream of ammonia it will give a steady flame of ten or twelve inches long.

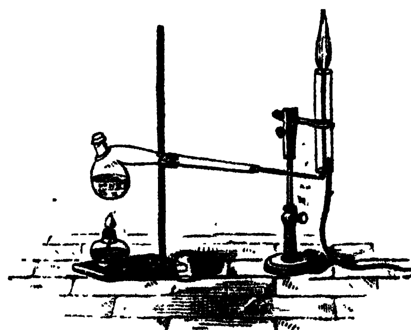


Fig. 146.

A similar experiment may be made with a smaller supply of oxygen, by lowering the tube delivering ammonia into a bottle or jar of oxygen, and applying a light to it just as it enters the mouth of the jar (fig. 147).

The elements of ammonia are easily separated from each other by passing the gas through a red-

hot tube, or still more readily by exposing it to the action of the high temperature of the electric spark, when the volume of the gas rapidly in-

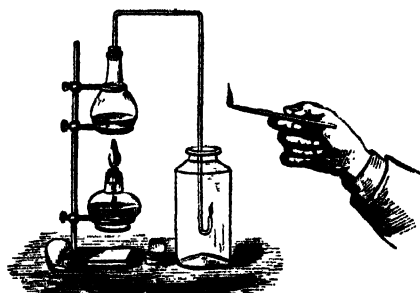


Fig. 147.

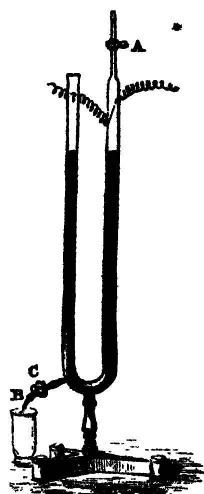


Fig. 148.

creases until it is exactly doubled, two volumes of ammonia being decomposed into 1 volume of nitrogen and 3 volumes of hydrogen.

For this experiment a measured volume of ammonia gas is confined over mercury (fig. 148), in a tube through which platinum wires are sealed for the passage of the spark from an induction-coil. The volume of the gas is doubled in a few minutes, and if the tube be furnished with a stop-cock (A), the presence of free hydrogen may be shown by filling the open limb with mercury and kindling the gas as it issues from the jet.*

As might be expected from its powerfully alkaline character, ammonia exhibits a strong attraction for acids, which it neutralises perfectly. If a bottle of ammonia gas, closed with a glass plate, be inverted over a similar bottle of hydrochloric acid gas, and the glass plates withdrawn (fig. 149), the gases will combine, with disengagement of much heat, forming a white solid, the hydrochlorate of ammonia ($NH_3.HCl$), in which the acid and alkali have neutralised each other. Again, if ammonia be added to diluted sulphuric acid, the latter will be entirely neutralised, and by evaporating the solution, crystals of the sulphate of ammonia ($2NH_3.H_2O.SO_3$) may be obtained.

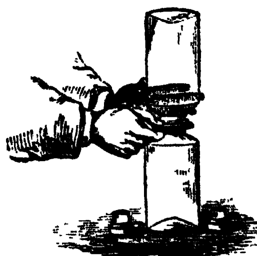


Fig. 149.

The substances thus produced by neutralising the acids with solution of ammonia bear a strong resemblance to the salts formed by neutralising the same acids with solutions of potash and soda, a circumstance which would encourage the idea that the solution of ammonia must contain an alkaline oxide similar to potash or soda.

Berzelius was the first to make an experiment which appeared strongly

* The eudiometer for passing electric sparks in rapid succession must have the platinum wires passed through the glass as shown in fig. 148, or it will be cracked by the heat of the sparks. The outlet tube B, closed by a small screw clamp C, pinching a caoutchouc connector, allows the mercury to be drawn off when necessary, to equalise the level in the two limbs.

to favour this view (commonly spoken of as the ammonium theory of Berzelius). The negative pole of a galvanic battery was placed in contact with mercury at the bottom of a vessel containing a strong solution of ammonia, in which the positive pole of the battery was immersed. Oxygen was disengaged at this pole, whilst the mercury in contact with the negative pole swelled to four or five times its original bulk, and became a soft solid mass, still preserving, however, its metallic appearance. So far, the result of the experiment resembles that obtained when hydrate of potash is decomposed under similar circumstances, the oxygen separating at the positive pole, and the potassium at the negative, where it combines with the mercury. Beyond this, however, the analogy does not hold; for in the latter case the metallic potassium can be readily separated from the mercury, whilst in the former, all attempts to isolate the ammonium have failed, for the soft solid mass resolves itself, almost immediately after its preparation, into mercury, ammonia (NH_3), and hydrogen, one atom of the latter being separated for each molecule of ammonia. This would also tend to support the conclusion, that a substance having the composition $NH_3 + H$ or NH_4 had united with the mercury; and since the latter is not known to unite with any non-metallic substance without losing its metallic appearance, it would be fair to conclude that the soft solid was really an amalgam of ammonium. However, the increase in the weight of the mercury is so slight, and the "amalgam," whether obtained by this or by other methods, is so unstable, that it would appear safer to attribute the swelling of the mercury to a physical change caused by the presence of the ammonia and hydrogen gases. It is difficult to believe that the solution of ammonia does really contain an oxide of ammonium ($2NH_3 + H_2O = (NH_4)_2O$), when we find it evolving ammonia so easily; but it is equally difficult, upon any other hypothesis, to explain the close resemblance between the salts obtained by neutralising acids with this solution, and those furnished by potash and soda.

The ordinary mode of exhibiting the production of the so-called *amalgam of ammonium* consists in acting upon the hydrochlorate of ammonia ($NH_3.HCl$), or *chloride of ammonium* (NH_4Cl), with the amalgam of sodium. A little pure mercury is heated in a test-tube, and a pellet of sodium thrown into it, when combination takes place with great energy. When the amalgam is nearly cool it may be poured into a larger tube containing a moderately strong solution of chloride of ammonium; the amalgam at once swells to many times its former bulk, forming a soft solid substance lighter than water, which may be shaken out of the tube as a cylindrical mass, decomposing rapidly with effervescence, evolving ammonia and hydrogen, and soon recovering its original volume and liquid condition.

88. *Atomic weight and volume of nitrogen.*—17 grains of ammonia have been proved to contain 14 grains of nitrogen combined with 3 grains of hydrogen. The latter gas being taken as the unit of atomic weight, the 3 grains would represent 3 atomic weights of hydrogen, and the question arises, How many atomic weights of nitrogen are represented by the 14 grains? On referring to the composition of ammonia by volume, we find that it furnishes three volumes of hydrogen for one volume of nitrogen when decomposed by the electric spark (p. 125), and hence it must contain one atom of nitrogen (14) and three atoms of hydrogen (3).

It will also be seen hereafter that the hydrogen in ammonia can be replaced by other bodies *in thirds*, showing that there must be three atoms of hydrogen present, whilst the 14 parts of nitrogen cannot be replaced in fractions, so that it must represent a single atom. The specific heat of hydrogen is found by experiment to be 13·5 times that of nitrogen, so that,

allowing for errors in determining it, 14 parts of nitrogen may be taken to be associated with the same amount of heat as one part of hydrogen (see 8).

89. *Determination of nitrogen in organic substances.*—An exact knowledge of the composition of ammonia is of great importance, because the general method of ascertaining the proportion of nitrogen present in animal and vegetable substances consists in converting that element into ammonia, which, being collected and weighed, furnishes by calculation the weight of nitrogen present.

To ascertain the proportion of nitrogen present in an organic substance, a weighed quantity of it is mixed with a large proportion of *soda-lime* (a mixture of hydrate of soda and hydrate of lime), and introduced into a tube of German glass (A, fig. 150) to which is attached, by a perforated cork, a bulb apparatus (B) containing hydrochloric acid. On heating the tube inch by inch with a charcoal or gas furnace, the nitrogen of the substance is evolved in combination with the hydrogen of the hydrates, in the form of ammonia, which is absorbed by the hydrochloric acid in the bulbs. When the whole length of the tube has been heated, the point (C) is nipped off, and air drawn through by applying suction to the orifice (D) of the bulb apparatus, so that all the ammonia may be carried into the hydrochloric acid. Its weight is then ascertained, either by evaporating the liquid in a weighed dish placed over a steam bath, and weighing the hydrochlorate of ammonia, or more accurately by converting it into the double chloride of platinum and ammonium. Sometimes a solution of sulphuric acid of known strength is substituted for the hydrochloric acid in the bulbs, and the weight of the ammonia is ascertained by determining the quantity of acid which has been neutralised.

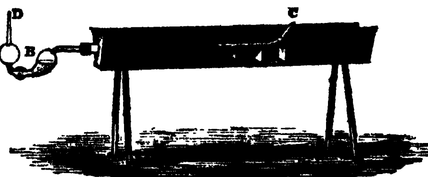
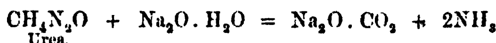


Fig. 150.—Estimation of nitrogen.

To illustrate the change which takes place when the organic substance is heated with the hydrates of soda and lime, let it be supposed that urea is the substance submitted to analysis.



$$\underset{\text{Urea.}}{CH_4N_2O} + Na_2O.H_2O = Na_2O.CO_2 + 2NH_3$$

The caustic soda alone would be too fusible and would corrode the glass too rapidly.

In the analysis of an organic substance containing carbon, hydrogen, nitrogen, and oxygen, the proportions of carbon and hydrogen having been ascertained by the method described at p. 80, and that of nitrogen by the process given above, the sum of the carbon, hydrogen, and nitrogen is deducted from the entire weight of the substance to obtain the proportion of oxygen. The weights thus found are divided by the atomic weights of the several elements to obtain the empirical formula, which is converted into a rational formula on the principle illustrated at p. 82.

For example, 10 grs. of urea were found to contain 2 grs. of carbon, 0·66 gr. of hydrogen, and 4·67 grs. of nitrogen.

10 grs. of urea *minus* 7·33 (carbon, hydrogen, and nitrogen) = 2·67 grs. of oxygen.

Dividing each of these numbers by the atomic weight of the element to which it refers, we have,

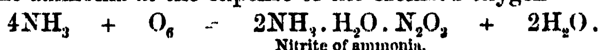
2·0 ÷ 12	=	0·165	atomic proportion of	carbon,
0·66 ÷ 1	=	0·66	„ „	hydrogen,
4·67 ÷ 14	=	0·33	„ „	nitrogen,
2·67 ÷ 16	=	0·165	„ „	oxygen,

leading to the empirical formula, in its simplest form, CH_4N_2O, for urea. But urea is an organic base, capable of uniting with acids to form salts,

and it is found that to neutralise one molecular weight (36·5 parts) of hydrochloric acid, 60 parts of urea are necessary. This quantity would contain 12 parts (one atom) of carbon, 4 parts (four atoms) of hydrogen, 28 parts (two atoms) of nitrogen, and 16 parts (one atom) of oxygen, so that the above formula would correctly represent the molecule of urea.

90. *Formation of ammonia in the rusting of iron.*—Although free nitrogen and hydrogen cannot be made to form ammonia by direct combination, this compound is produced when the nitrogen meets with hydrogen in the *nascent* state; that is, at the instant of its liberation from a combined form. Thus, if a few iron filings be shaken with a little water in a bottle of air, so that they may cling round the sides of the bottle, and a piece of red litmus paper be suspended between the stopper and the neck, it will be found to have assumed a blue colour in the course of a few hours, and ammonia may be distinctly detected in the rust which is produced. It appears that the water is decomposed by the iron, in the presence of the carbonic acid of the air and water, and that the hydrogen liberated enters at once into combination with the nitrogen, held in solution by the water, to form ammonia.

91. *Production of nitrous and nitric acids from ammonia.*—If a few drops of a strong solution of ammonia be poured into a pint bottle, and ozonised air (from the tube for ozonising by induction, fig. 48) be passed into the bottle, thick white clouds will speedily be formed, consisting of *nitrite of ammonia*, the nitrous acid having been produced by the oxidation of the ammonia at the expense of the ozonised oxygen—



$$4NH_3 + O_6 = \underset{\text{Nitrite of ammonia.}}{2NH_3 . H_2O . N_2O_3} + 2H_2O.$$

If copper filings be shaken with solution of ammonia in a bottle of air, white fumes will also be produced, together with a deep blue solution containing oxide of copper and nitrite of ammonia; the act of oxidation of the copper appearing to have induced a simultaneous oxidation of the ammonia.



Fig. 151.

A coil of thin platinum wire made round a pencil, if heated to redness at the lower end and suspended in a flask (fig. 151) with a little strong ammonia at the bottom, will continue to glow for a great length of time, in consequence of the combination of the ammonia with the oxygen of the air taking place at its surface, attended with great evolution of heat. Thick white clouds of nitrite of ammonia are formed, and frequently red vapour of nitrous acid (N_2O_3) itself.

If a tube delivering oxygen gas be passed down to the bottom of the flask (fig. 152), the action will be far more energetic, the heat of the platinum rising to whiteness, when an explosion of the mixture of ammonia and oxygen will ensue. After the explosion the action will recommence, so that the explosion will repeat itself as often as may be wished. It is unattended with danger if the mouth of the flask be pretty large. By regulating the stream of oxygen, the bubbles of that gas may be made to burn as they pass through the ammonia at the bottom of the flask.



Fig. 152.

The oxidation of ammonia may also be shown by the arrangement represented in fig. 153. Air is slowly passed, from the gas-bag B, through very weak ammonia in the bottle *a*, into a hard glass tube having a piece of red litmus paper at *b*, and a plug of platinised asbestos in the centre, heated by a gas-burner; a piece of blue litmus paper

is placed at *c*, and the tube is connected with a large globe (*d*). The red litmus at *b* is changed to blue by the ammonia, whilst the blue litmus at *c* is reddened by the nitrous acid produced in its oxidation, and clouds of nitrite of ammonia, accompanied by red nitrous fumes, appear in *d*.

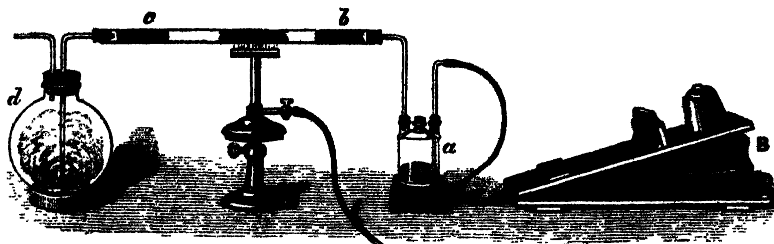


Fig. 153.—Oxidation of ammonia.

(The burner represented in the figure is a Bunsen burner (p. 103), surmounted by a T-piece with several holes.)

In the presence of strong bases, and of porous materials to favour oxidation, ammonia appears to be capable of suffering further oxidation and conversion into nitric acid, which combines with the base to form a nitrate, thus—



$$2NH_3 + CaO + O_8 = \underset{\text{Nitrate of lime.}}{CaO . N_2O_5} + 3H_2O .$$

This formation of nitrates from ammonia is commonly referred to as *nitrification*, and appears to play an important part in the formation of the natural supplies of saltpetre which are of so great importance to the arts.*

COMPOUNDS OF NITROGEN AND OXYGEN.

92. Though these elements in their pure state exhibit no attraction for each other, five compounds, which contain them in different proportions, have been obtained by indirect processes.

When a succession of strong electric sparks from the induction coil is passed through atmospheric air in a flask (especially if the air be mixed with oxygen), a red gas is formed in small quantity, which is either nitrous acid (N_2O_3) or nitric peroxide (NO_2).

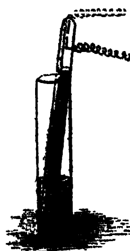


Fig. 154.

If the experiment be made in a graduated eudiometer (fig. 154), standing over water coloured with blue litmus, the latter will very soon be reddened by the acid formed, and the air will be found to diminish very considerably in volume, eventually losing its power of supporting combustion, in consequence of the removal of oxygen.

When hydrogen gas, mixed with a small quantity of nitrogen, is burnt, the water collected from it is found to have an acid taste and reaction, due to the presence of a little nitric acid, resulting from the combination of the nitrogen with the oxygen of the air under the influence of the intense heat of the hydrogen flame.

Since all the compounds of nitrogen and oxygen are obtained, in practice, from hydrated nitric acid, the chemical history of that substance must precede that of the oxides of nitrogen.

* The charcoal which has been used in the sewer ventilators (see p. 64) has been found to contain abundance of nitrates.

NITRIC ACID.

93. This most important acid is obtained from saltpetre, which is found as an incrustation upon the surface of the soil in hot and dry climates, as in some parts of India and Peru. The salt imported into this country from Bengal and Oude consists of nitrate of potash (KNO_3), whilst the Peruvian or Chilian saltpetre is nitrate of soda ($NaNO_3$). Either of these will serve for the preparation of nitric acid.

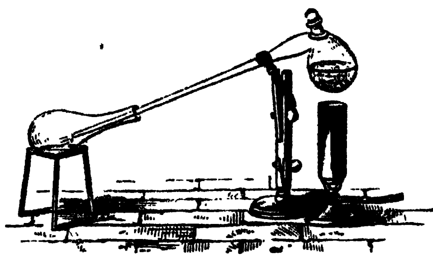


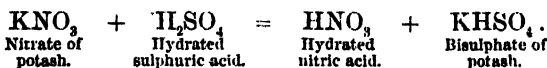
Fig. 155.- Preparation of nitric acid.

On the small scale, in the laboratory, nitric acid is prepared by distilling nitrate of potash with an equal weight of concentrated sulphuric acid.

In order to make the experiment, four ounces of powdered nitre, thoroughly dried, may be introduced into a pint-stoppered retort (fig. 155), and two and a half measured ounces of concentrated sulphuric acid poured upon it. As soon as the acid has soaked into the nitre, a gradually increasing heat may be applied by means of an Argand burner, when the acid will distil over. It must be preserved in a stoppered bottle.

When the acid has ceased distilling, the retort should be allowed to cool, and filled with water. On applying a moderate heat for some time, the saline residue will be dissolved. The solution may then be poured into an evaporating dish, and evaporated down to a small bulk. On allowing the concentrated solution to cool, crystals of bisulphate of potash ($KHSO_4$) are deposited, a salt which is very useful in many metallurgic and analytical operations.

The decomposition of nitrate of potash by an equal weight of concentrated sulphuric acid is explained by the equation—



$$\underset{\text{Nitrate of potash.}}{KNO_3} + \underset{\text{Hydrated sulphuric acid.}}{H_2SO_4} = \underset{\text{Hydrated nitric acid.}}{HNO_3} + \underset{\text{Bisulphate of potash.}}{KHSO_4}.$$

It would appear at first sight that one-half of the sulphuric acid might be dispensed with, but it is found that when less sulphuric acid is employed, so high a temperature is required to effect the complete decomposition of the saltpetre (the above equation then representing only the first stage of the action), that much of the nitric acid is decomposed; and the neutral sulphate of potash (K_2SO_4), which would be the final result, is not nearly so easily dissolved out of the retort by water as the bisulphate.

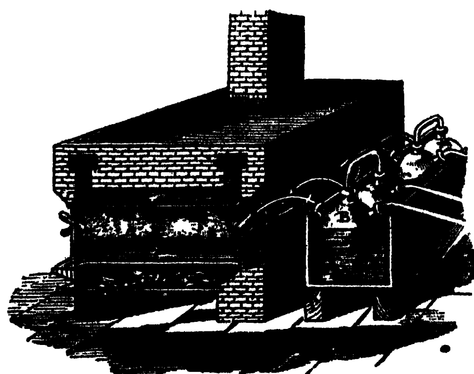
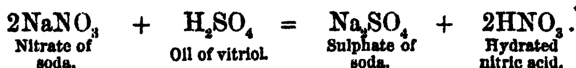


Fig. 156. -Preparation of nitric acid.

For the preparation of large quantities of nitric acid, the nitrate of soda is substituted for nitrate of potash, being much cheaper, and furnishing a larger proportion of nitric acid.

The nitrate of soda is introduced into an iron cylinder (A, fig. 156), lined with fire-clay to protect it from the action of the acid, and half its weight of sulphuric acid (oil of vitriol) is poured upon it. Heat is then applied by a furnace, into which the cylinders are built, in pairs, when the hydrated nitric acid passes off in vapour, and is condensed in a series of stoneware bottles (B), surrounded with cold water.

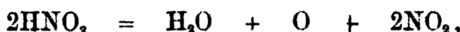


$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

Nitrate of soda. Oil of vitriol. Sulphate of soda. Hydrated nitric acid.

The sulphate of soda left in the retort is useful in the manufacture of glass.

In the preparation of nitric acid, it will be observed at the beginning and towards the end of the operation, that the retort becomes filled with a red vapour. This is due to the decomposition by heat of a portion of the colourless vapour of nitric acid, into water, oxygen, and nitric peroxide—



$$2HNO_3 = H_2O + O + 2NO_2,$$

this last forming the red vapour, a portion of which is absorbed by the hydrated nitric acid, and gives it a yellow colour. The pure nitric acid is colourless, but if exposed to sunlight it becomes yellow, a portion suffering this decomposition. In consequence of the accumulation of the oxygen in the upper part of the bottle, the stopper is often forced out suddenly when the bottle is opened, and care must be taken that drops of this very corrosive acid be not spirted into the face.

The strongest nitric acid (obtained by distilling perfectly dry nitre with an equal weight of pure oil of vitriol, and collecting the middle portion of the acid separately from the first and last portions, which are somewhat weaker) emits very thick grey fumes when exposed to damp air, because its vapour, though itself transparent, absorbs water very readily from the air, and condenses into very minute drops of diluted nitric acid which compose the fumes. The weaker acids commonly sold in the shops do not fume so strongly. An exact criterion of the strength of any sample of the acid is afforded by the specific gravity, which may be ascertained by the methods described at page 122, using a hydrometer adapted for liquids heavier than water. Thus, the strongest acid (HNO_3) has the specific gravity 1·52;* whilst the ordinary *aquafortis* or diluted nitric acid has the sp. gr. 1·29, and contains only 46·6 per cent. of HNO_3. The concentrated nitric acid usually sold by the operative chemist (*double aquafortis*) has the sp. gr. 1·42, and contains 67·6 per cent. of HNO_3.

A very characteristic property of nitric acid is that of staining the skin yellow. It produces the same effect upon most animal and vegetable matters, especially if they contain nitrogen. The application of this in dyeing silk of a fast yellow colour may be seen by dipping a skein of white silk in a warm mixture of concentrated nitric acid with an equal volume of water, and afterwards immersing it in dilute ammonia, which will convert the yellow colour into a brilliant orange. When sulphuric or hydrochloric acid is spilt upon the clothes, a red stain is produced, and a little ammonia restores the original colour; but nitric acid stains are yellow, and ammonia intensifies instead of removing them, though it prevents the cloth from being eaten into holes.

Nitric acid changes most organic colouring matters to yellow, but, unless very concentrated, it merely reddens litmus. If solutions of indigo and

* It is extremely difficult to obtain the HNO_3 free from any extraneous water, as it undergoes decomposition not only when vaporised at the boiling point, but even at ordinary temperatures.

litmus are warmed in separate flasks, and a little nitric acid added to each, the indigo will become yellow and the litmus red. Here the indigo (C_8H_5NO) acquires oxygen from the nitric acid, and is converted into *isatine* ($C_8H_5NO_2$).

When hydrated nitric acid is heated, it begins to boil at 184° F., but it cannot be distilled unchanged, for a considerable quantity is decomposed into nitric peroxide, oxygen, and water, the two first passing off in the gaseous form, whilst the water remains in the retort with the nitric acid, which thus becomes gradually more and more diluted, until it contains 68 per cent. of HNO_3, when it passes over unchanged at the temperature of 248° F. The specific gravity of this acid is 1·42. If an acid weaker than this be submitted to distillation, water will pass off until acid of this strength is obtained, when it distils over unchanged.

The specific gravity of the vapour of nitric acid, at 187° F., has been determined as 29·6 (H = 1), which is sufficiently near to half of 63 to show that the molecule HNO_3 would occupy exactly two volumes if it had not suffered partial decomposition by heat.

The facility with which hydrated nitric acid parts with a portion of its oxygen, renders it very valuable as an *oxidising agent*. Comparatively few substances which are capable of forming compounds with oxygen can escape oxidation when treated with nitric acid.

A small piece of phosphorus dropped into a porcelain dish containing the strongest nitric acid (and placed at some distance to avoid danger), soon begins to act upon the acid, generally with such violence as to burst out into flame, and sometimes to shatter the dish ; the result of this action is hydrated phosphoric acid, the same compound which is formed in the anhydrous state, when phosphorus is burnt in oxygen gas.

When sulphur is heated with nitric acid, it is actually oxidised to a greater extent than when burnt in pure oxygen, for in this case it is converted into sulphurous acid (SO_2), whilst nitric acid imparts to it three atoms of oxygen, forming sulphuric acid (SO_3).

Charcoal, which is so unalterable by most chemical agents at the ordinary temperature, is oxidised by nitric acid. If the strongest nitric acid be poured upon finely powdered charcoal, the latter takes fire at once.

Even iodine, which is not oxidised by free oxygen, is converted into iodic acid (I_2O_5) by nitric acid.

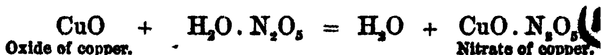
It not unfrequently happens in this manner that oxygen, in a state of unstable combination, is more prone to unite with other substances than when it is in a free state. It would seem that the disposition to combination having been once impressed upon it is retained, so as to facilitate its union with other bodies.

But it is especially in the case of metals that the oxidising powers of nitric acid are called into useful application.

Acids are not capable of forming salts with metals, but only with their oxides. Hence, when a metal is dissolved by any oxygen acid, the latter must first convert the metal into an oxide, which then acts upon the acid to form a salt.

For the purpose of facilitating the explanation of the action of nitric acid upon metals, it will be found convenient to represent the hydrated nitric acid by the formula $H_2O.N_2O_5$ (= $2HNO_3$), for which it will be presently seen that some justification is afforded by the fact that it may be produced by dissolving anhydrous nitric acid (N_2O_5) in water.

If a little black oxide of copper be heated in a test-tube with nitric acid, it dissolves, without evolution of gas, yielding a blue solution, which contains the nitrate of copper. In this case the oxide of copper may be represented as having simply displaced the water of the hydrated acid—



$$\underset{\text{Oxide of copper.}}{CuO} + H_2O.N_2O_5 = H_2O + \underset{\text{Nitrate of copper.}}{CuO.N_2O_5}$$

But when nitric acid is poured upon metallic copper (copper turnings), a very violent action ensues, red fumes are abundantly evolved, and the metal dissolves in the form of nitrate of copper—



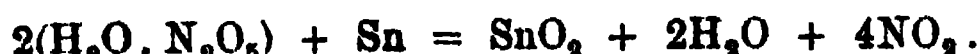
$$4(H_2O.N_2O_5) + Cu_3 = \underset{\text{Nitrate of copper.}}{3(CuO.N_2O_5)} + 4H_2O + \underset{\text{Nitric oxide.}}{2NO}.$$

The nitric oxide itself is colourless, but as soon as it comes into contact with the oxygen of the air, it is converted into the red nitric peroxide, $NO + O = NO_2$.

All the metals in common use are acted upon by nitric acid, except gold and platinum, so that this acid is employed to distinguish and separate these metals from others of less value. The ordinary ready method of ascertaining whether a trinket is made of gold consists in touching it with a glass stopper wetted with nitric acid, which leaves gold untouched, but colours base alloys blue, from the formation of nitrate of copper. The *touch-stone* allows this mode of testing to be applied with greater accuracy. It consists of a species of black basalt, obtained chiefly from Silesia. If a piece of gold be drawn across its surface, a golden streak is left, which is not affected by moistening with nitric acid; whilst the streak left by brass, or any similar base alloy, would be rapidly dissolved by the acid. Experience enables an operator to determine by means of the touch-stone pretty nearly the amount of gold present in the alloy, comparison being made with the streaks left by alloys of known composition.

Though all the metals in common use, except gold and platinum, are *oxidised* by nitric acid, they are not all *dissolved;* there are two metals, tin and antimony, which are left by the acid in the state of insoluble oxides, which possess acid properties, and do not unite with the nitric acid.

If some concentrated nitric acid be poured upon tin filings, no action will be observed;* but on adding a little water, red fumes will be evolved in abundance, and the tin will be converted into a white powder, which is the binoxide of tin (SnO_2), *putty powder*. The gas which is evolved in this case is the nitric peroxide (NO_2), and the action of the acid is represented by the equation which follows :—



$$2(H_2O.N_2O_5) + Sn = SnO_2 + 2H_2O + 4NO_2.$$

If the white mixture of binoxide of tin with nitric acid be made into a paste with slaked lime, the smell of ammonia will be exhaled; and experiments with other metals have shown it to be a general principle, that when any metal capable of decomposing water is dissolved in diluted nitric acid, ammonia is always formed, its quantity increasing with the degree of dilution of the nitric acid; of course, the ammonia combines with the excess of acid present to form nitrate of ammonia, and the lime was added in the above experiment in order to displace the ammonia from its combination, and to exhibit its odour. This conversion of nitric acid into ammonia becomes the more interesting when it is remembered that the ammonia can be reconverted into nitric acid (p. 129).

By dissolving zinc in very diluted nitric acid, a very large quantity of ammonia may be obtained. The change is easily followed if we suppose the *nascent* hydrogen

* It is a fact which has scarcely been explained in a satisfactory manner, that the concentrated nitric acid often refuses to act upon metals which are violently attacked by the diluted acid.

(or hydrogen with the tendency to combination still remaining impressed upon it, see p. 132), produced by the action of the zinc upon the water, to act upon the nitric acid, converting its oxygen into water, and its nitrogen into ammonia, thus—$HNO_3 + H_8 = 3H_2O + NH_3$. The exalted attractions possessed by substances in the nascent state, that is, at the instant of their passing from a state of combination, are very remarkable, and will be found to receive frequent application.*

Action of nitric acid upon organic substances.—The oxidising action of nitric acid upon some organic substances is so powerful as to be attended with inflammation; if a little of the strongest nitric acid be placed in a porcelain capsule, and a few drops of oil of turpentine be poured into it from a test-tube fixed to the end of a long stick, the turpentine takes fire with a sort of explosion. By boiling some of the strongest acid in a test-tube (fig. 157), the mouth of which is loosely stopped with a plug of raw silk or of horse-hair, the latter may be made to take fire and burn brilliantly in the vapour of nitric acid.

In many cases the products of the action of nitric acid exhibit a most interesting relation to the substances from which they have been produced, one or more atoms of the hydrogen of the original compound having been removed in the form of water by the oxygen of the nitric acid, whilst the spaces thus left vacant have been filled up by the nitric peroxide resulting from the deoxidation of the nitric acid, producing what is termed a *nitro-substitution* compound. A very simple example of this displacement of H by NO_2 is afforded by the action of nitric acid upon benzole. A little concentrated nitric acid is placed in a flask, and benzole cautiously dropped into it; a violent action ensues, and the acid becomes of a deep red colour; if the contents of the flask be now poured into a large vessel of water, a heavy yellow oily liquid is separated, having a powerful odour, like that of bitter almond oil. This substance, which is used to a considerable extent in perfumery under the name of essence of mirbane, is called *nitro-benzole*, and its formula, $C_6H_5(NO_2)$, at once exhibits its relation to benzole, C_6H_6.†

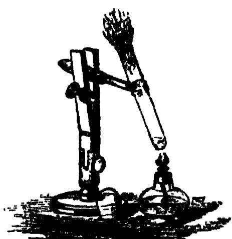


Fig. 157.

But the change does not stop here, for by continuing the action of the acid, *dinitro-benzole* $C_6H_4 2(NO_2)$ is obtained, in which two atoms of hydrogen have been displaced by nitric peroxide.

It is by an action of this description that nitric acid gives rise to gun-cotton, and other explosive substances of the same class, when acting upon the different varieties of woody fibre, as cotton, paper, sawdust, &c.

The preparation and composition of gun-cotton will be described hereafter.

94. The oxidising effects of nitric acid are not confined to the free acid, but are shared to some extent by the nitrates. A mixture of nitrate of

* When a solution of nitrate of potash is mixed with a strong solution of caustic potash, and heated with granulated zinc, ammonia is abundantly disengaged, being produced from the nitric acid by the nascent hydrogen resulting from the action of the zinc upon the caustic potash.

Recent experiments have indicated the existence of substances intermediate between the nitric acid and the ammonia into which it is finally converted. One of these, named *hydroxylamine*, NH_3O, has been examined. It is a well-defined base, forming crystalline salts with the acids.

† $C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O$.
$C_6H_6 + 2(HNO_3) = C_6H_4 2(NO_2) + 2H_2O$.

lead with charcoal explodes when sharply struck, from the sudden evolution of carbonic acid produced by the oxidation of the carbon. If a few crystals of nitrate of copper be sprinkled with water and quickly wrapped up in tin-foil, the latter will, after a time, be so violently oxidised as to emit brilliant sparks.

But in the case of bases which retain the nitric acid with greater force, such as the alkalies, the oxidation takes place only at a high temperature. If a little nitre be fused in an earthen crucible or an iron ladle, and, when it is at a red heat, some powdered charcoal, and afterwards some flowers of sulphur, be thrown into it, the energy of the combustion will testify to the violence of the oxidation. In this manner the carbon is converted into carbonate of potash ($K_2O.CO_2$), and the sulphur into sulphate of potash ($K_2O.SO_3$). See *Gunpowder.*

Combining weight of nitric acid.—Experiment proves that 56 parts by weight (1 molecule) of caustic potash are neutralised by 63 parts of hydrated nitric acid, and this quantity of the acid is found to contain 1 part of hydrogen, 14 parts of nitrogen, and 48 parts (3 atoms) of oxygen. Hence the formula of the acid is written HNO_3.

95. *Anhydrous nitric acid* or *nitric anhydride* (N_2O_5) is obtained by gently heating nitrate of silver in a slow current of chlorine, great care being taken to exclude every trace of water—



$$\underset{\text{Nitrate of silver.}}{Ag_2O \,.\, N_2O_5} + Cl_2 = \underset{\text{Chloride of silver.}}{2AgCl} + O + \underset{\text{Nitric anhydride.}}{N_2O_5}\,.$$

The anhydride is condensed as a crystalline solid in a receiver cooled with ice and salt. It forms transparent colourless prisms which liquefy at 85° F., and boil at 113°. By a slightly higher temperature it is readily decomposed; and it has been said to decompose, even at the ordinary temperature, in sealed tubes which were shattered by the evolved gas.

When the anhydride is brought in contact with water, much heat is evolved, and hydrated nitric acid is produced.

The specific gravity of the vapour of anhydrous nitric acid being unknown, it is only a surmise that its molecule is represented by N_2O_5. Its formation by the action of chlorine upon nitrate of silver appears to take place in two stages; (1) $Ag.NO_2.O + Cl_2 = AgCl + NO_2Cl$ (*chloride of azotyle*) + O and (2) $NO_2Cl + Ag.NO_2.O = AgCl + NO_2.NO_2.O$ (anhydrous nitric acid.)

The disposition of HNO_3 to give NO_2 as a product of its decomposition, and to exchange it for the hydrogen of organic substances, leads to the belief that it is really formed upon the type of a molecule of water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, in which half the hydrogen is displaced by NO_2. The relation between the anhydrous and the hydrated acid and the nitrates would then be a very simple one; anhydrous nitric acid, $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$; hydrated nitric acid, $\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O$; saltpetre, $\left.\begin{matrix}K\\NO_2\end{matrix}\right\}O$.

Nitrates.—Its attraction for bases places nitric acid among the strongest of the acids, though the disposition of its elements to assume the gaseous state at high temperatures, conjoined with the feeble attraction existing between nitrogen and oxygen, causes its salts to be decomposed, without exception, by heat.

The nature of the decomposition varies with the base contained in the nitrate. The nitrates of very powerful bases (such as the alkalies) are first converted into nitrites by the action of heat; thus $K_2O.N_2O_5$ gives $K_2O.N_2O_3$ and O_2; the nitrites themselves being eventually decomposed, evolving nitrogen and oxygen, and leaving the uncombined base. The nitrates of feebler bases (such as oxide of copper and oxide of lead) evolve nitric peroxide (NO_2) and oxygen, the base being left, unless it be decom-

posible by heat, as is the case with the oxides of silver and mercury, when the metal itself will be separated. As a general rule, the nitrates are easily soluble in water.

As in the case of the carbonates, the nitrates may be represented either by substitutive formulæ, representing them as derived from one or more molecules of HNO_3 by the substitution of metals for the hydrogen, or by additive formulæ, as composed of the metallic oxides combined with the anhydrous nitric acid N_2O_5. Generally speaking, the additive formulæ are more convenient for explaining the decompositions in which these salts take part.

Comparatively few of the nitrates are in common use; the following table contains those most frequently used:—

Chemical Name.	Common Name.	Additive Formula.	Substitutive Formula.
Nitrate of pot ash	Nitre, saltpetre	$K_2O \cdot N_2O_5$	KNO_3
Nitrate of soda	Cubic nitre / Peruvian saltpetre	$Na_2O \cdot N_2O_5$	$NaNO_3$
Nitrate of strontia	Nitrate of strontian	$SrO \cdot N_2O_5$	$Sr(N_3)_2$
Basic nitrate of bismuth	Trisnitrate of bismuth / Flake white	$Bi_2O_3 \cdot N_2O_5 \cdot H_2O$	
Nitrate of silver	Lunar caustic	$Ag_2O \cdot N_2O_5$	$AgNO_3$

96. *Nitrous oxide* or *laughing gas* (N_2O = 44 parts by weight = 2 vols.) is prepared by heating nitrate of ammonia, when it is resolved into water and nitrous oxide.*



$$NH_3 \cdot HNO_3 = 2H_2O + N_2O \,.$$

Nitrate of ammonia is obtained by adding fragments of carbonate of ammonia to nitric acid† diluted with an equal volume of water, until the carbonate no longer effervesces in the liquid, which is then evaporated down until a drop solidifies on a cold surface, when the whole may be poured out upon a clean stone, and the mass broken up and preserved in a well-stoppered bottle, because it is liable to attract moisture from the air. To obtain the nitrous oxide, an ounce of the salt may be gently heated in a small retort, when it melts, boils, and gradually disappears entirely in the forms of steam and nitrous oxide. The latter may be collected, with slight loss, over water.

Nitrous oxide is perfectly colourless, but has a slight odour and a sweetish taste. Its characteristic intoxicating property is well known. It accelerates the combustion of a taper like oxygen itself, and will even kindle into flame a spark at the end of a match. It can readily be distinguished from oxygen, however, by shaking it with water, which absorbs, at the ordinary temperature, about three-fourths of its volume of the nitrous oxide. It is also much heavier than oxygen, its specific gravity being 1·53, and is not a permanent gas, being liquefied by a pressure of 40 atmospheres at 45° F., and solidified at −150° F. It is now sold in a liquid state in wrought iron vessels for use as an anæsthetic in dental surgery.

* By passing the mixture of nitrous oxide and aqueous vapour over hydrate of potash at a dull red heat, nitric acid and ammonia are reproduced.

† Which must remain clear when tested with nitrate of silver, showing it to be free from chlorine.

The liquid nitrous oxide possesses properties similar to those of liquid carbonic acid with respect to its rapid evaporation; but it may be drawn into test-tubes in a liquid state from the receiver. A lighted match thrown into the liquid burns with great brilliancy. When mixed with bisulphide of carbon and evaporated *in vacuo*, it produces the lowest temperature hitherto obtained—220° F.

97. *Nitric oxide* (NO = 30 parts by weight = 2 vols.) is usually obtained by the action of copper upon diluted nitric acid—



$$4(H_2O.N_2O_5) + Cu_3 = 3(CuO.N_2O_5) + 2NO \quad 4H_2O.$$

300 grains of copper turnings or clippings are introduced into a retort, and three measured ounces of a mixture of concentrated nitric acid with an equal volume of water are poured upon them. A very gentle heat may be applied to assist the action, and the gas may be collected over water (see fig. 158), which absorbs the red fumes (NO_2) formed by the union of the NO with the air contained in the retort.

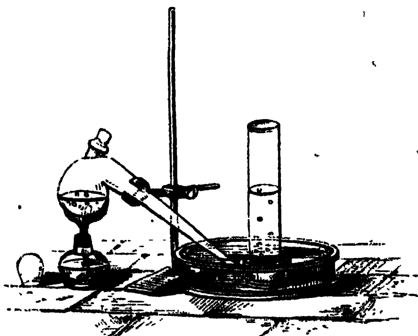


Fig. 158.

Nitric oxide is distinguished from all other gases by the production of a red gas, when the colourless nitric oxide is allowed to come in contact with uncombined oxygen, the presence of which, in mixtures of gases, may be readily detected by adding a little nitric oxide. The red gas consists chiefly of nitric peroxide (NO_2), but it often contains also some (N_2O_3) nitrous acid.

The combination of nitric oxide with oxygen may be exhibited by decanting a pint bottle of oxygen, under water, into a tall jar filled with water coloured with blue litmus, and adding to it a pint bottle of nitric oxide (fig. 159). Strong red fumes are immediately produced, and on gently agitating the cylinder, the fumes are absorbed by the water, reddening the litmus. The oxygen will now have been reduced to half its volume, and if another pint of nitric oxide be added, the remainder of the oxygen will be absorbed, showing that *two volumes of nitric oxide combine with one volume of oxygen*, forming the nitric peroxide which is absorbed by the water.

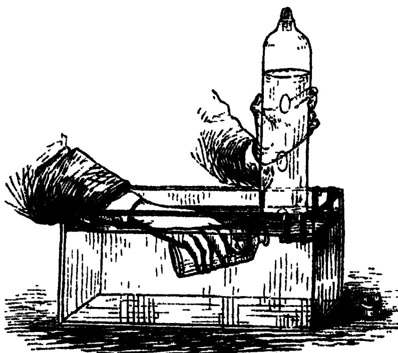
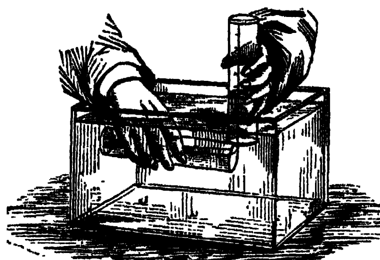


Fig. 159.

The addition of nitric oxide to atmospheric air was one of the earliest methods employed for removing the oxygen in order to determine the composition of air; but important variations were observed in the results, in consequence of the occasional formation of N_2O_3 in addition to the NO_2.

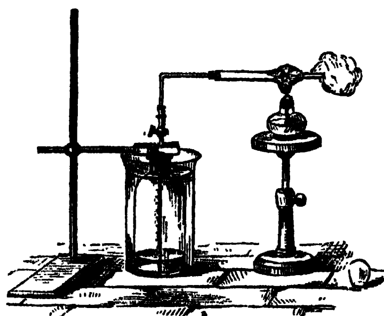
The rough analysis of air by this method may be instructively performed with two similar gas cylinders, each divided into ten equal volumes. Into one are introduced five volumes of air, and into the other five volumes of nitric oxide. On decanting

the air, under water, into the nitric oxide (fig. 160), the red nitric peroxide will be formed and absorbed by the water, the ten volumes of gas shrinking to seven, showing that three volumes have been absorbed, of which one volume would of course represent the oxygen contained in the five volumes of air.


Fig. 160.

The nitric oxide prepared by the action of copper on nitric acid generally contains nitrous oxide, and will seldom give correct results in the above experiment. Pure nitric oxide may be obtained by heating in a retort 100 grains of nitrate of potash, 1000 grains of sulphate of iron, and three measured ounces of diluted sulphuric acid (containing one measure of acid to three measures of water), which will yield above two pints of the gas.*

In all its properties, nitric oxide is very different from nitrous oxide. It is much lighter, having almost exactly the same specific gravity as air, viz., 1·04, has never yet been liquefied, and is not dissolved to any important extent by water. When a lighted taper is immersed in nitric oxide, it is extinguished, although this gas contains twice as much oxygen as nitrous oxide, which so much accelerates the combustion of a taper; for the elements are held together by a stronger attraction in the nitric oxide, so that its oxygen is not so readily available for the support of combustion. (The nitric oxide prepared from copper and nitric acid sometimes contains so much nitrous oxide that a taper burns in it brilliantly.) Even phosphorus, when just kindled, is extinguished in nitric oxide, but when allowed to attain to full combustion in air, it burns with extreme brilliancy in the gas. Indeed, nitric oxide appears to be the least easy of decomposition of the whole series of oxides of nitrogen, which accounts for it being the most common result of the decomposition of the other oxides. Nitrous oxide itself, when passed through a red-hot tube, is partly converted into nitric oxide; and when a taper burns in a bottle of nitrous oxide, the upper part of the bottle is often filled with a red gas, indicating the formation of nitric oxide, and its oxidation by the air entering the bottle.


Fig. 161.

The difference in the stability of the two gases is also shown by their behaviour with hydrogen. A mixture of nitrous oxide with an equal volume of hydrogen explodes when in contact with flame, yielding steam and nitrogen, but a mixture of equal volumes of nitric oxide and hydrogen burns quietly in air, the hydrogen not decomposing the nitric oxide. An excess of hydrogen, however, is capable of decomposing nitric oxide, ammonia and water being formed.

If two volumes of nitric oxide be mixed with five volumes of hydrogen, and the gas passed through a tube having a bulb filled with platinised asbestos (fig. 161),†

* $K_2O.N_2O_5 + 6(FeO.SO_3) + 4(H_2O.SO_3) = K_2O.SO_3 + 3(Fe_2O_3.3SO_3) + 2NO + 4H_2O$.

† Asbestos which has been wetted with solution of bichloride of platinum, dried, and heated to redness, to reduce the platinum to the metallic state.

the mixture issuing from the orifice of the tube will produce the red vapours, by contact with the air, which will strongly redden blue litmus; but if the platinised asbestos be heated with a spirit-lamp, the hydrogen, encouraged by the action of the platinum (91) will decompose the nitric oxide, and strongly alkaline vapours of ammonia will be produced, restoring the blue colour to the reddened litmus: $NO + H_5 = NH_3 + H_2O$. It will be remembered that when oxygen is in excess, ammonia is converted, under the influence of platinum, into water and nitrous acid (91).

Nitric oxide is readily absorbed by ferrous salts (salts of protoxide of iron) with which it forms dark brown solutions. If a little solution of sulphate of iron be shaken in a cylinder of nitric oxide closed with a glass plate, the gas will be immediately absorbed, and the solution will become dark brown. On applying heat, the brown compound is decomposed. A compound of 4 molecules of ferrous sulphate and one molecule of nitric oxide has been obtained in small brown crystals, which lose all their nitric oxide *in vacuo*.

98. *Nitrous acid* (N_2O_3 = 76 parts by weight).*—This acid is said to exist, as nitrite of ammonia, in minute quantity, in rain water, and is occasionally found in combination with alkalies or alkaline earths, in well-waters, where it has probably been formed by the oxidation of ammonia (91). Small quantities of nitrite of ammonia appear to be formed by the combustion in air of gases containing hydrogen, this element uniting with the atmospheric oxygen and nitrogen.

Nitrous acid may be obtained by heating starch with nitric acid, but the most convenient process consists in gently heating nitric acid (sp. gr. 1·35) with an equal weight of arsenious acid, and passing the gas, first through a U-tube (fig. 162) surrounded with cold water, to condense un-

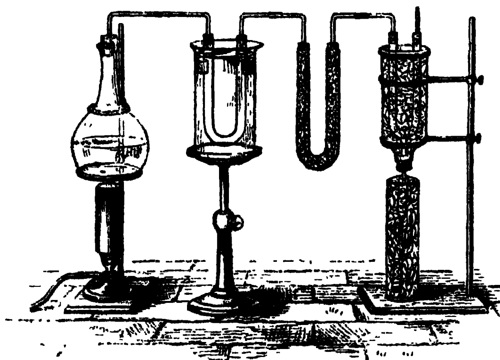
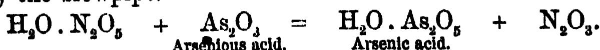


Fig. 162.—Preparation of nitrous acid.

decomposed nitric acid, then through a similar tube containing chloride of calcium, to absorb aqueous vapour, and afterwards into a U-tube surrounded with a freezing mixture of ice and salt. Through a small tube opening into the bend of this U-tube, the condensed nitrous acid drops into a tube drawn out to a narrow neck, so that it may be drawn off, and sealed by the blowpipe.



$$H_2O \,.\, N_2O_5 \quad + \underset{\text{Arsenious acid.}}{As_2O_3} = \underset{\text{Arsenic acid.}}{H_2O \,.\, As_2O_5} \quad + \quad N_2O_3.$$

The nitrous acid is thus obtained as a blue liquid which boils below 32° F., becoming converted into a red vapour, and partly decomposed into NO and NO_2. Water at about 32° F. dissolves the acid without

* The specific gravity of nitrous acid not having been ascertained on account of its want of stability, the formula N_2O_3 is only provisionally assigned to the molecule.

decomposing it, yielding a blue solution which is decomposed, as the temperature rises, into nitric acid which remains in the liquid, and nitric oxide which escapes with effervescence—



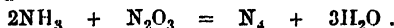
$$3N_2O_3 + H_2O = H_2O.N_2O_5 + 4NO.$$

A very dilute solution of nitrous acid may be preserved for some time without decomposition.

The salts of nitrous acid, or *nitrites*, are interesting on account of their production from the nitrates by the action of heat (p. 135).

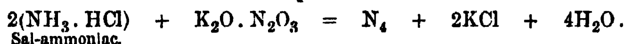
If nitrate of potash be fused in a fire-clay crucible and heated to redness, it will evolve bubbles of oxygen, and slowly become converted into nitrite of potash ($K_2O.N_2O_3$). The heat should be continued until a portion removed on the end of an iron rod, and dissolved in water, gives a strongly alkaline solution. The fused mass may then be poured upon a *dry* stone, and when cool, broken into fragments and preserved in a stoppered bottle. On heating a fragment of the nitrite of potash with diluted sulphuric acid, red vapours will be disengaged, but these contain little nitrous acid, the greater part of this being decomposed by the water into nitric acid and nitric oxide.

When nitrous acid acts upon ammonia, both compounds suffer decomposition, water and nitrogen being the results—



$$2NH_3 + N_2O_3 = N_4 + 3H_2O.$$

This is sometimes taken advantage of in preparing nitrogen gas by boiling mixed solutions of sal-ammoniac and nitrite of potash—



$$\underset{\text{Sal-ammoniac.}}{2(NH_3.HCl)} + K_2O.N_2O_3 = N_4 + 2KCl + 4H_2O.$$

In experiments upon organic compounds, nitrous acid is sometimes employed as a convenient agent for effecting simultaneously the removal of three atoms of hydrogen from a compound, and the insertion of one atom of nitrogen.

When solutions of nitrites are heated in contact with air, they gradually absorb oxygen, becoming converted into nitrates.

99. *Nitric peroxide* (NO_2 = 46 parts by weight = 2 vols.), also called *hyponitric acid* and *peroxide of nitrogen* or *pernitric oxide*: formerly known as *nitrous acid*.—By passing a mixture of nitric oxide with half its volume of oxygen, free from every trace of moisture, into a perfectly dry tube cooled in a mixture of ice and salt, the dark red gas is condensed into colourless prismatic crystals, which melt at 10° F. into a nearly colourless liquid. This gradually becomes yellow as the temperature rises, and at the ordinary temperature has a deep orange colour. It is very volatile, boiling at 71° F., and being converted into a red-brown vapour, which was long mistaken for a permanent gas, on account of the great difficulty of condensing it when once mixed with air or oxygen. Nitric peroxide is also obtained, mixed with one-fourth of its volume of oxygen, by heating the nitrate of lead (fig. 163)—



$$PbO.N_2O_5 = PbO + 2NO_2 + O.$$

The vapour of nitric peroxide is much heavier than atmospheric air.

Its specific gravity (compared with hydrogen at the same temperature) diminishes as the temperature rises. At 275° F. it is 23 times as heavy as hydrogen, showing its molecular weight to be 46. This variation in density, in conjunction with the other changes, with increase of temperature, lead to the belief that the molecule of nitric peroxide, at low temperatures (in its liquid state), is N_2O_4, and becomes decomposed into $2NO_2$ at high temperatures.

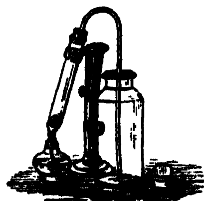


Fig. 163.—Preparation of nitric peroxide.

Its colour varies with the temperature, becoming very dark at 100° F. The smell of the vapour is very characteristic. It supports the combustion of strongly burning charcoal or phosphorus, and

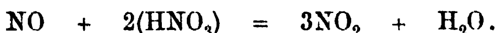
oxidises most of the metals, potassium taking fire in it spontaneously. The nitric peroxide must, therefore, rank as a powerful oxidising agent, and it is the presence of this substance in the red fuming nitric acid that imparts to it higher oxidising powers than those of the colourless nitric acid.

The so-called *nitrous acid* of commerce is really nitric acid holding in solution a large proportion of nitric peroxide, and is prepared by introducing sulphur into the retorts containing the mixture of nitrate of soda and sulphuric acid employed in the preparation of the nitric acid, a portion of which is deoxidised and converted into nitric peroxide. Water immediately decomposes the nitric peroxide into nitric oxide and nitric acid—



$$3NO_2 + H_2O = NO + 2HNO_3.$$

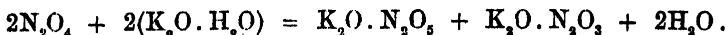
When water is gradually added to liquid nitric peroxide, it effervesces, from escape of nitric oxide, and becomes green, blue, and ultimately colourless. The production of the green and blue colours appears to be due to the formation of N_2O_3 in an intermediate decomposition; $2N_2O_4 + H_2O = N_2O_3 + 2HNO_3$; and when this is decomposed by an excess of water, the liquid, of course, becomes colourless. If the red nitric acid of commerce be gradually diluted with water, it will be found to undergo similar changes, always becoming colourless at last. The nitric acid which has been used in a Grove's battery always has a green colour from the large amount of nitric peroxide which has accumulated in it, in consequence of the decomposition of the acid by the hydrogen disengaged during the action of the battery; $H + HNO_3 = H_2O + NO_2$. If this green acid be diluted with a little water, it becomes blue, and a larger quantity of water renders it colourless, causing the evolution of nitric oxide. Similar colours are obtained by passing nitric oxide into nitric acid of different degrees of concentration, apparently because nitric peroxide is formed and dissolved by the acid—



$$NO + 2(HNO_3) = 3NO_2 + H_2O.$$

When silver, mercury, and some other metals are dissolved in cold nitric acid, a green or blue colour is often produced, leading a novice to suspect the presence of copper, the colour being really caused by the solution in the unaltered nitric acid of the nitric peroxide produced by the deoxidation of another portion.

Nitric peroxide was formerly believed to be an independent acid capable of forming salts. It is true that its vapours have a strongly acid reaction to test-papers, but when brought into contact with bases, it produces a mixture of nitrate and nitrite—



$$2N_2O_4 + 2(K_2O.H_2O) = K_2O.N_2O_5 + K_2O.N_2O_3 + 2H_2O.$$

100. *General review of the oxides of nitrogen.*—All the above oxides of nitrogen are directly obtainable from nitric acid by the action of metals; but since the result of such action varies much with the temperature and state of concentration of the acid, it cannot be depended upon for the preparation of the oxides in a separate state.

Nitric peroxide is the chief product of the action of tin upon nitric acid—



$$2(H_2O.N_2O_5) + Sn = 2H_2O + 4NO_2 + SnO_2.$$

Nitrous acid is abundantly formed when silver is acted on by nitric acid—



$$3(H_2O \,.\, N_2O_5) + Ag_4 = 3H_2O + N_2O_3 + 2(Ag_2O \,.\, N_2O_5).$$

Nitric oxide has been shown to be evolved when nitric acid is deoxidised by copper—



$$4(H_2O \,.\, N_2O_5) + Cu_3 = 4H_2O + 2NO + 3(CuO \,.\, N_2O_5);$$

though, if the acid be concentrated or the temperature high, nitrous oxide and nitrogen are mixed with the nitric oxide.

Nitrous oxide is given off when zinc is dissolved in nitric acid diluted with ten measures of water—



$$5(H_2O \,.\, N_2O_5) + Zn_4 = 5H_2O + N_2O + 4(ZnO \,.\, N_2O_5);$$

the nitrous oxide, however, is mixed with nitric oxide.

Nitric oxide, nitrous acid, and nitric peroxide, are very remarkable for their relations to oxygen. Nitric oxide is one of the very few substances which combine with dry oxygen at the ordinary temperature, and yet the nitric peroxide which is thus produced is very ready to yield its oxygen to other substances. Nitrous acid, as might be expected, is intermediate in this respect, being capable of acting as a reducing agent upon powerfully oxidising substances, and as an oxidising agent upon substances having a great attraction for oxygen. Thus, a solution of nitrite of potash, acidified with sulphuric acid, will bleach permanganate of potash, reducing the permanganic acid (Mn_2O_7) to manganous oxide (MnO; whilst, if added to sulphate of iron, the nitrite converts the ferrous oxide (FeO) into ferric oxide (Fe_2O_3), and this solution, which was capable of reducing the permanganate of potash before, is now found to be without effect upon it, unless an excess of the nitrite has been added.

The oxides of nitrogen, as illustrating combination in multiple proportions by weight and volume.—In its most general form, the *law of multiple proportions* may be thus stated. When a substance (A) combines with another substance (B) in more than one proportion, the quantities of B, which combine with *a constant quantity* of A, are multiples of the smallest combining quantity of B by some whole number.

In the oxides of nitrogen this law is exemplified in the simplest form, since the quantities of oxygen which combine with a constant quantity of nitrogen, are multiples of the least combining quantity of oxygen by 2, 3, 4, and 5.

		N.	O.
Nitrous oxide,	N_2O	28	16
Nitric oxide (two molecules),	N_2O_2	28	16×2
Nitrous acid,	N_2O_3	28	16×3
Nitric peroxide,	N_2O_4	28	16×4
Nitric acid,	N_2O_5	28	16×5

It was shown, at p. 126, that there is ground for representing the atomic weight of nitrogen as = 14.

When *nitrous oxide* is passed through a red-hot porcelain tube, its volume is increased by one-half, and the resulting gas is found to be a mixture of one volume of oxygen and two volumes of nitrogen. Hence it is inferred that, in nitrous oxide, two volumes or atoms (28 parts) of nitrogen are united with one volume or atom (16 parts) of oxygen, to form two volumes or one molecule of nitrous oxide (representing 44 parts by weight).

When charcoal is strongly heated in *nitric oxide*, the volume of the gas remains unchanged; but it is found, on analysis, to have become converted into a mixture of equal volumes of carbonic acid and nitrogen ($2NO + C = CO_2 + N_2$). Since one volume of carbonic acid contains one volume of oxygen (page 88), the experiment

proves that one volume of oxygen and one volume of nitrogen exist in two volumes of nitric oxide, or that one atom of nitrogen (or 14 parts) is combined with one atom of oxygen (16 parts) in two volumes (one molecule, or 30 parts by weight) of nitric oxide.

The direct evidence of the composition of *nitrous acid* is not so satisfactory as that in the two preceding cases. This acid has been obtained, however, by the direct union of one volume of oxygen with four volumes of nitric oxide, leading to the conclusion that it contains N_2O_3. Its molecular weight has been determined by the analysis of nitrite of silver, which was found to contain, for one molecule (232 parts by weight) of oxide of silver, 76 parts by weight of nitrous acid, representing a compound of 28 parts by weight of nitrogen (or two atoms = 2 volumes), with 48 parts by weight (or three atoms = 3 volumes) of oxygen. The volume occupied by the molecule of nitrous acid in the state of vapour has not yet been ascertained, no accurate determination of the specific gravity of its vapour having been made.

Nitric peroxide has been analysed by passing the vapour produced from a known weight of the liquid over red-hot metallic copper, which absorbed the oxygen, leaving the nitrogen to be collected and measured. It was thus found that 14 parts by weight (one atom = 1 volume) of nitrogen were combined with 32 parts by weight (two atoms = 2 volumes) of oxygen, a result which is confirmed by the direct union of 2 volumes of NO (one molecule) with 1 volume of oxygen (one atom) to form NO_2.

Nitric anhydride, or anhydrous nitric acid, was analysed by a method similar to that employed for nitric peroxide, and was found to contain 28 parts by weight (two atoms) of nitrogen, combined with 80 parts (five atoms) of oxygen. The volume occupied by the molecule of nitric anhydride in the state of vapour has not been determined, on account of the want of stability of this compound.

The facility with which nitrous acid and nitric peroxide can be decomposed with formation of nitric oxide, renders it probable that they really contain that compound. To express this, they may plausibly be represented as formed after the same plan as a molecule of water. Just as in $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, the two atoms of hydrogen are linked together by the diatomic oxygen, so in nitrous acid, $\left.\begin{matrix}NO\\NO\end{matrix}\right\}O$, two molecules of nitric oxide are linked together by the atom of oxygen, whilst in nitric peroxide (N_2O_4) a molecule of NO is bound up with a molecule of NO_2, thus $\left.\begin{matrix}NO\\NO_2\end{matrix}\right\}O$. If nitric acid be represented by $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$, it is easy to understand the behaviour of these three oxides with the alkalies. Thus, by the action of nitrous acid on caustic potash, we obtain nitrate of potash $\left.\begin{matrix}K\\NO\end{matrix}\right\}O$, whilst nitric acid gives nitrate of potash, $\left.\begin{matrix}K\\NO_2\end{matrix}\right\}O$, and nitric peroxide gives a mixture of both salts.

CHLORINE.

Cl = 35·5 parts by weight = 1vol. 35·5 grs. = 46·7 cub. in. at 60° F. and 30" Bar., 35·5 grms. = 11·2 litres at 0° C. and 760 mm. Bar.

101. This element is never found in the uncombined state, but is very abundant in the mineral world in the forms of chloride of sodium (common salt) and chloride of potassium. In these forms also it is an important constituent of the fluids of the animal body, but as it is not found in sufficient proportion in vegetable food, or in the solid parts of animal food, a quantity of salt must be added to these in order to form a wholesome diet. Chloride of sodium is indispensable as a raw material for several of the most useful arts, such as the manufactures of soap and glass, bleaching, &c., in fact, it is the source of three of the most generally useful chemical products, viz., chlorine, hydrochloric acid, and soda.

About the middle of the seventeenth century, a German chemist, named Glauber, distilled some common salt with sulphuric acid, and obtained a strongly acid liquid to which he gave the name *muriatic acid* (from *muria*, *brine*) and which was proved to be identical with the acid long known to

the alchemists as *spirit of salt*. The saline mass which was left after the experiment was then termed Glauber's salt, but afterwards received its present name of sulphate of soda.

It was undoubtedly a natural inference from this experiment that common salt was composed of muriatic acid and soda, and that the sulphuric acid had a greater attraction for the soda than the muriatic acid, which was therefore displaced by it. In accordance with this view, common salt was called muriate of soda, without further question, until the year 1810, when the experiments of Davy proved that it was really composed of the two elementary substances, chlorine and sodium, and must therefore be styled, as it now is, chloride of sodium, and represented by the formula NaCl. It was further shown by Davy, that the muriatic acid was really composed of chlorine and hydrogen, and that it was, in fact, chloride of sodium (NaCl) in which the sodium had been displaced by hydrogen (HCl).

Preparation of chlorine.—In order to extract chlorine from common salt, it is heated with black oxide of manganese and diluted sulphuric acid; the acid decomposes the binoxide of manganese, part of the oxygen of which displaces the chlorine from the chloride of sodium, yielding soda which combines with the sulphuric acid, so that the sulphates of soda and manganese are left in solution, and chlorine escapes in the form of gas;



$$2NaCl + MnO_2 + 2(H_2O \,.\, SO_3) = Na_2O \,.\, SO_3 + MnO \,.\, SO_3 + 2H_2O + Cl_2 \,.$$

600 grains of common salt may be mixed with 450 grains of binoxide of manganese, introduced into a retort (fig 164), and a cold mixture of $1\frac{1}{2}$ oz. by measure of strong sulphuric acid with 4 oz. of water poured upon it. The retort having been well

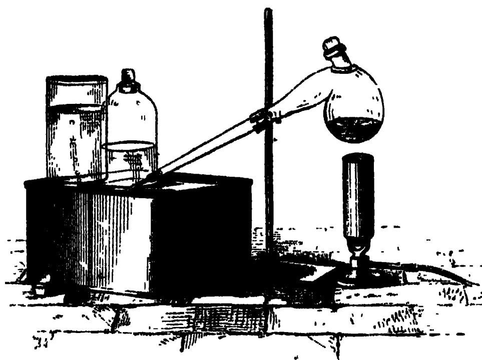


Fig. 164.—Preparation of chlorine.

shaken to wet the powder thoroughly with the acid, a very gentle heat is applied, and the gas collected in bottles filled with water and inverted in the pneumatic trough. When the bottles are filled, the stoppers, previously greased, must be inserted into them under water. The first bottle or two will contain the air from the retort, and will therefore have a paler colour than the pure chlorine afterwards collected. It is advisable to keep a jar filled with water standing ready on the shelf of the trough, so that any excess of chlorine may be passed into it instead of being allowed to escape into the air, causing serious inconvenience. The bottles of moist chlorine must always be preserved in the dark. Chlorine may also be conveniently prepared by gently heating 500 grains of binoxide of manganese with 4 oz. (measured) of common hydrochloric acid—



$$MnO_2 \quad + \quad 4HCl \quad = \quad MnCl_2 \quad + \quad 2H_2O \quad + \quad Cl_2 \,.$$

Either of the above methods will furnish about five pints of chlorine.

In *Weldon's process* for the manufacture of chlorine, the manganese is made to act as a carrier of oxygen from the atmosphere to the hydrogen of the hydrochloric acid, setting the chlorine free. For this purpose, the chloride of manganese obtained in the above process is decomposed by lime; $MnCl_2 + CaO = CaCl_2 + MnO$. By mixing the MnO with more lime, and blowing atmospheric air through the mixture, MnO_2 is reproduced, and may be employed for decomposing a fresh quantity of HCl. In *Deacon's* process, a mixture of air and hydrochloric acid gas is passed over heated fire-brick which has been soaked in solution of sulphate of copper and dried. The final result is expressed by the equation $2HCl + (N_4 + O) = H_2O + Cl_2 + N_4$, so that the chlorine obtained is mixed with twice its volume of nitrogen, which is stated, however, not to interfere seriously with its useful application. The action of the copper-salt has not been clearly explained, but it appears to depend upon the instability of the chlorides of copper under the influence of heat and oxygen.

Properties of chlorine.—The physical and chemical properties of chlorine are more striking than those of any element hitherto considered. Its colour, whence it derives its name (χλωρός, pale green) is bright greenish yellow, its odour insupportable. It is twice and a half as heavy as air (sp. gr. 2·47), and may be reduced to the liquid state by a pressure of only four atmospheres at 60° F. If a bottle of chlorine be held mouth downwards in water, its stopper removed, one-third of the chlorine decanted into a jar, and the rest of the gas shaken with the water in the bottle, the mouth of which is closed by the palm of the hand (fig. 165), the water will absorb twice its volume of chlorine, producing a vacuum in the bottle, which will be held firmly against the hand by atmospheric pressure. If air be then allowed to enter, and the bottle again shaken as long as any absorption takes place, a saturated solution of chlorine (*chlorine water*) will be obtained. By exposing this yellow solution to a temperature approaching 32° F., yellow crystals of *hydrate of chlorine* ($Cl.5H_2O$) are obtained, the liquid becoming colourless.



Fig. 165.

When the water in the pneumatic trough, over which chlorine is being collected, happens to be very cold, the gas is often so foggy as to be quite opaque, in consequence of the deposition of minute crystals of the hydrate. On standing, the gas becomes clear, crystals of the hydrate being deposited like hoar-frost upon the sides of the bottle; the gas also becomes clear when the bottles are slightly warmed.

The hydrate of chlorine affords a convenient source of liquid chlorine. A number of bottles of saturated solution of chlorine, prepared as above, are exposed on a cold winter's day until the hydrate has crystallised. The crystals are thrown upon a filter, cooled to nearly 32°, allowed to drain, and rammed into a pretty strong tube closed at one end, about twelve inches long, and half an inch in diameter, previously cooled in ice or snow. The tube having been nearly filled with the crystals, is kept surrounded with snow, whilst its upper end is gradually softened in the blowpipe flame and drawn off so as to be strongly sealed. When this tube is immersed in water at 100° F., the chlorine separates from the water, and two layers of liquid are formed, the lower one consisting of amber-yellow liquid chlorine (sp. gr. 1·33), and the upper, about three times its volume, of a pale yellow aqueous solution of chlorine. On allowing the tube to cool again, the crystalline hydrate is reproduced, even at common temperatures, being more permanent under pressure. It may even be sublimed in a sealed tube.

Liquid chlorine may also be obtained in a state in which it can be preserved, by disengaging the chlorine in a sealed tube (as in the liquefaction of ammonia) from about 200 grains of bichloride of platinum previously dried at 400° F. The bichloride is heated with a spirit-lamp in one limb of the tube, whilst the other is immersed in a freezing mixture. The face and hands of the operator should be protected against the bursting of the tube.

The most characteristic chemical feature of chlorine is its powerful

attraction for many other elements at the ordinary temperature. Among the non-metals, hydrogen, bromine, iodine, sulphur, selenium, phosphorus, and arsenic, combine spontaneously with chlorine, and nearly all the metals behave in the same way.

If a piece of dry phosphorus be placed in a deflagrating spoon, and immersed in a bottle of chlorine (fig. 166), it will take fire spontaneously, combining with the chlorine to form terchloride of phosphorus (PCl_3). A tall glass shade may be placed over the bottle, which should stand in a plate containing water, so that the fumes may not escape into the air.

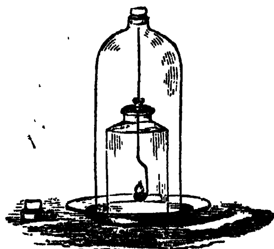


Fig. 166.

If phosphorus be placed in a bottle of oxygen to which a small quantity of chlorine has been added, it will burst out after a minute or two into most brilliant combustion.

Powdered antimony (the metal, not the sulphide), sprinkled into a bottle of chlorine (fig. 167), descends in a brilliant shower of white sparks, the antimony burning in the chlorine to form terchloride of antimony ($SbCl_3$). A little water should be placed at the bottom of the bottle to prevent it from being cracked, and the fumes should be restrained by a shade standing in water.

If a flask, provided with a stop-cock (fig. 168), be filled with leaves of *Dutch metal* (an alloy of copper and zinc, resembling gold leaf), exhausted of air, and screwed on to a capped jar of chlorine standing over water, it will be found, on opening the

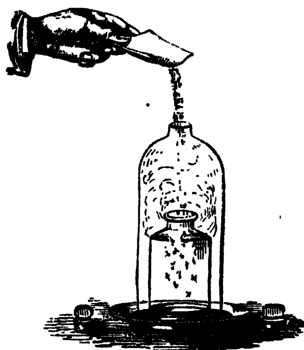


Fig. 167.

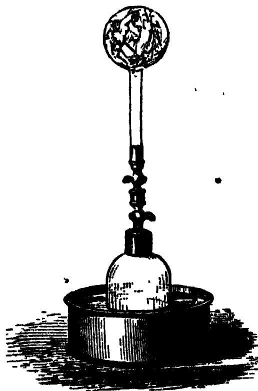


Fig. 168.

stop-cocks so that the chlorine may enter the flask, that the metal burns with a red light, forming thick yellow fumes containing chloride of copper ($CuCl_2$) and chloride of zinc ($ZnCl_2$) If gold leaf be suspended in chlorine, it will not be immediately attacked, but will gradually become converted into terchloride of gold ($AuCl_3$).

102. The most important useful applications of chlorine depend upon its powerful chemical attraction for hydrogen. The two gases may be mixed without combining, if kept in the dark, but when the mixture is exposed to light, they combine to form hydrochloric acid gas (HCl), with a rapidity proportionate to the intensity of the *actinic* rays (or rays capable of inducing chemical change) in the light employed. Exposed to gas-light or ordinary diffused daylight, the hydrogen and chlorine combine slowly, but direct sunlight causes sudden combination, attended with explosion,

resulting from the expansion which the hydrochloric acid formed suffers by the heat evolved in the act of combination. The light of magnesium burning in air, and some other artificial lights, also cause sudden combination.

Two pint gas-bottles should be ground so that their mouths may be fitted accurately to each other, and filled respectively with dry hydrogen and dry chlorine, both gases having been dried by passing through oil of vitriol, and collected, the hydrogen by upward, and the chlorine by downward, displacement of air. The mouths should be slightly greased before the bottles are filled with gas, and afterwards closed with glass plates. On placing the bottles together, and removing the plates so that the gases may come in contact (see fig. 149), the yellow colour of the chlorine will be permanent as long as the mixture is kept in the dark, but on exposure to daylight the colour will gradually disappear, the hydrochloric acid gas being colourless. If the bottles be now closed with glass plates, the small quantity of gas which escapes during the operation will be seen to fume strongly in air, a property not possessed either by hydrogen or chlorine, and when the necks of the bottles are immersed in water and the glass plates withdrawn, the water will rapidly absorb the gas, and be forced into the bottles so as to fill them, with the exception of a small space occupied by the air accidentally admitted, showing that the hydrochloric acid gas possesses the joint volumes of the hydrogen and chlorine. If the water be tinged with blue litmus it will be strongly reddened as it enters the bottles.

The sudden union of the gases with explosion may be safely exhibited in a Florence flask. The flask is filled with water, which is then poured out into a measure. Exactly half the water is returned to the flask, and its level in the latter carefully marked with a diamond or file. The flask having been again filled with water, is closed with the thumb and inverted in the pneumatic trough, so that hydrogen may be passed up into it to displace one-half of the water. A short-necked funnel is then inserted, under the water, into the neck of the flask, and chlorine rapidly decanted up from a gas-bottle (fig. 169) until the rest of the water has been displaced. The flask is now raised from the water and quickly closed with a cork (fig. 170), through which pass two gutta-percha-covered copper wires, the ends of which have been stripped and brought sufficiently near to each other to allow of the passage of the electric spark within the flask. The ends external to the flask are also stripped and bent into hooks for convenient connexion with the conducting wires. The flask is placed upon the ground, and covered with a wooden box to prevent the pieces from flying about. On connecting the copper wires with the conducting wires from an induction-coil or an electrical machine, it will be heard, on passing the spark, that the mixture has violently exploded; on raising the box it will be found filled with strong fumes of hydrochloric acid, and a heap of small fragments of glass will represent the flask.

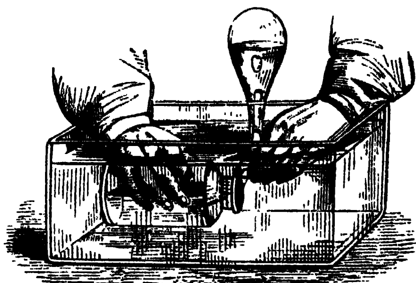


Fig. 169.

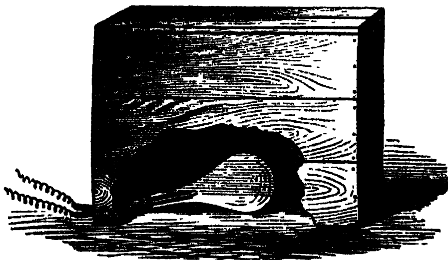


Fig. 170.

A flask filled in the same way with the mixture of hydrogen and chlorine may be attached to the end of a long stick, and thrust out into the sunlight, when it explodes with great violence.

To illustrate the direct combination of hydrogen and chlorine under the influ-

ence of artificial light, it is better to employ the mixture of exactly equal volumes of the two gases obtained by decomposing hydrochloric acid by the galvanic current. The voltameter (A, fig. 171) is filled with concentrated hydrochloric acid, and its conducting wires (B) connected with the terminals of a Grove's battery of five or six cells. Chlorine is at once evolved at the positive pole (or that connected with the platinum in the battery), and hydrogen at the negative pole (attached to the zinc of the battery). It is advisable to place the voltameter in a vessel of cold water, to prevent the hydrochloric acid from becoming too hot. The gas evolved during the first five minutes should be allowed to pass into a waste-jar, because, until the liquid becomes saturated with chlorine, the evolved gas does not contain exactly equal volumes of the constituent elements. A very thin glass bulb (C), about 2 inches in diameter, blown upon a stout piece of tube, the ends of which have been drawn out to narrow open points (fig. 172), is then connected with the voltameter by means of a caoutchouc tube. A similar caoutchouc tube is attached to the free end of the bulb. When the colour of the gas in the bulb (which should be shaded from sunlight) shows that it is completely filled, the caoutchouc tubes are well closed by nipper-taps (fig. 173), and the bulb detached from the voltameter. In this condition it may be kept in the dark for a long time without alteration or escape of gas. The mixture may be most effectively exploded by exposing it to the flash of light evolved by firing a mixture of nitric oxide gas with vapour of bisulphide of carbon.* For this purpose a cylinder may be filled with nitric oxide (page 137) over water, closed with a glass plate, and placed mouth upwards upon the table; the glass plate being lifted for an instant, a few drops of bisulphide of carbon are poured into the cylinder, which is then shaken. The bulb containing the explosive mixture is suspended at some distance from the operator, and the gas cylinder is placed within a few inches of it

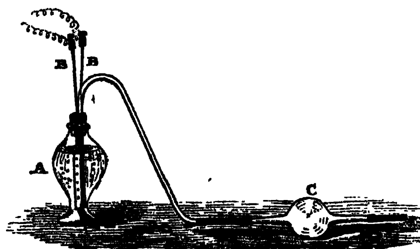


Fig. 171.



Fig. 172.

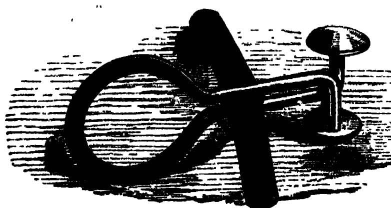


Fig. 173.

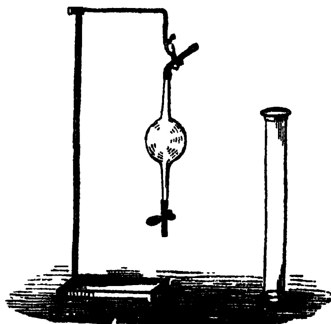


Fig. 174.

(fig. 174). On applying a light to the cylinder, the flash will cause the immediate explosion of the mixture in the bulb, with production of strong fumes of hydrochloric acid.

If the bulb be thin, no injury will be inflicted by the pieces of glass, or the operator may easily protect his face by a screen.

The attraction of chlorine for hydrogen enables it to effect the decom-

* A mixture of equal volumes of chlorine and hydrogen may be exploded in a *strong* cylinder by the light of a piece of magnesium tape. The cylinder should be only partly filled with the mixture, and firmly held with its mouth only just beneath the water in the trough.

position of water. The solution of chlorine in water may be preserved in the dark without change; but when exposed to light it loses the smell of chlorine, and becomes converted into weak hydrochloric acid, the oxygen being liberated; $H_2O + Cl_2 = 2HCl + O$.* The decomposition takes place much more quickly at a red heat, so that oxygen is obtained in abundance by passing a mixture of chlorine and steam through a red-hot tube.

For this experiment a porcelain tube is employed, which is bound round with sheet copper to prevent it from cracking, and loosely filled with fragments of broken porcelain to expose a large heated surface. This tube is gradually heated to redness in a charcoal furnace (fig. 175). One end of it receives the mixture of chlorine with steam, obtained by passing the chlorine evolved from hydrochloric acid and binoxide of manganese in A (p. 144), through a flask (B) of boiling water. The other end of the tube is connected with a bottle (C) containing solution of potash to absorb any excess of chlorine and the hydrochloric acid formed; from this bottle the oxygen is collected over the pneumatic trough.

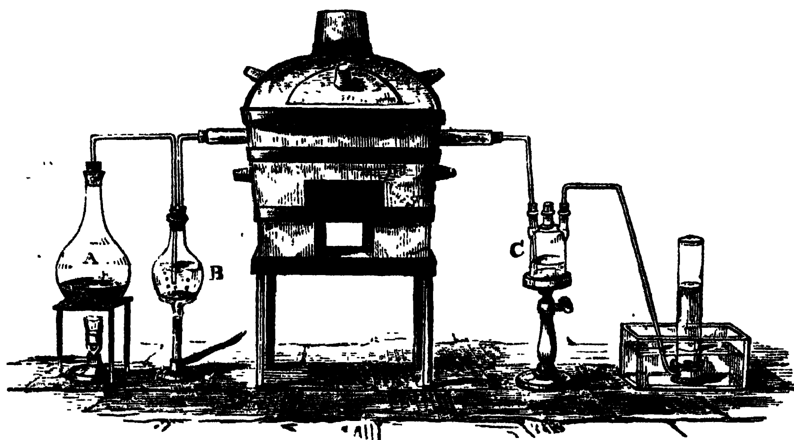


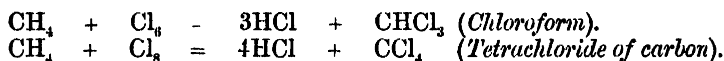
Fig. 175.—Steam decomposed by chlorine.

Since water is decomposed by chlorine, it is not surprising that most other hydrogen compounds are attacked by it. Ammonia (NH_3) is acted upon with great violence. If a stream of ammonia gas issuing from a tube connected with a flask in which solution of ammonia is heated (see fig. 147) be passed into a bottle of chlorine, it takes fire immediately, burning with a peculiar flame, and yielding thick white clouds of hydrochlorate of ammonia; $4NH_3 + Cl_3 = 3(NH_3.HCl) + N$. A piece of folded filter-paper dipped in strong ammonia, and immersed in a bottle of chlorine, will exhibit the same effect. When the chlorine is allowed to act upon hydrochlorate of ammonia, its operation is less violent, and one of the most explosive substances is produced, which was formerly believed to be a *chloride of nitrogen*, but is probably a compound formed by the removal of a part of the hydrogen from ammonia, and the introduction of chlorine in its stead.

* A portion of this oxygen combines with chlorine, producing hypochlorous acid, and, as recently stated, perchloric acid.

Many of the compounds of hydrogen with carbon are also decomposed with violence by chlorine. When a piece of folded filter-paper is dipped into oil of turpentine ($C_{10}H_{16}$), and afterwards into a bottle of chlorine, it bursts into a red flame, liberating voluminous clouds of carbon and hydrochloric acid. Acetylene (C_2H_2) was found to explode spontaneously with chlorine when exposed to light (page 91). The striking decomposition of olefiant gas (C_2H_4) by chlorine on the approach of a flame has already been noticed (page 93). When a lighted taper is immersed in chlorine, it continues to burn, but with a small red flame, the hydrogen only of the wax combining with the chlorine, whilst the carbon separates in black smoke, mixed with the hydrochloric fumes. When chlorine is brought in contact with the flame of a spirit-lamp, it renders the flame luminous by causing the separation of solid particles of carbon (page 100). It has been seen, in the case of olefiant gas, that chlorine sometimes combines directly with the hydrocarbons.

When marsh-gas (CH_4) is diluted with an equal bulk of carbonic acid, to prevent violent action, and four volumes of chlorine added for each volume of marsh-gas, an oily liquid is gradually formed under the influence of daylight. This oily liquid is a mixture of chloroform and bichloride of carbon, the production of which is explained by the following equations:—

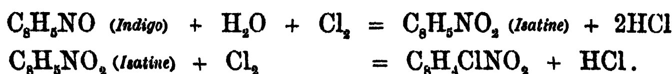


$$CH_4 + Cl_6 = 3HCl + CHCl_3 \text{ (Chloroform).}$$
$$CH_4 + Cl_8 = 4HCl + CCl_4 \text{ (Tetrachloride of carbon).}$$

It is evident from these equations that chlorine is capable, not only of removing hydrogen from a compound, but also of taking its place, atom for atom—a mode of action which gives rise to a very large number of chlorinated products from organic substances.

The attraction of chlorine for hydrogen enables the moist gas to act as an oxidising agent. Thus, if marsh-gas and chlorine be mixed in the presence of water, and exposed to daylight, the water is decomposed, its hydrogen combining with the chlorine, and its oxygen with the carbon of the marsh-gas; $CH_4 + 2H_2O + Cl_8 = CO_2 + 8HCl$.

103. The powerful bleaching effect of chlorine upon organic colouring matters is now easily understood. If a solution of chlorine in water be poured into solution of indigo (*sulphindigotic acid*) the blue colour of the indigo is discharged, and gives place to a comparatively light yellow colour. The presence of water is essential to the bleaching of indigo by chlorine, the dry gas not affecting the colour of dry indigo. The indigo is first oxidised at the expense of the water and converted into *isatine*, which is then acted upon by the chlorine and converted into *chlorisatine*, having a brownish yellow colour—



$$C_8H_5NO \text{ (Indigo)} + H_2O + Cl_2 = C_8H_5NO_2 \text{ (Isatine)} + 2HCl$$
$$C_8H_5NO_2 \text{ (Isatine)} + Cl_2 = C_8H_4ClNO_2 + HCl.$$

Nearly all vegetable and animal colouring matters contain carbon, hydrogen, nitrogen, and oxygen, and are converted by moist chlorine into products of oxidation or chlorination which happen to be colourless, or nearly so.

*, That dry chlorine will not bleach, may be shown by shaking some oil of vitriol in

a bottle of the gas, and allowing it to stand for an hour or two, so that the acid may remove the whole of the moisture. If a piece of crimson paper be dried at a moderate heat and suspended in the bottle while warm, it will remain unbleached for hours; but a similar piece of paper suspended in a bottle of moist chlorine will be bleached almost immediately. If characters be written on crimson paper with a wet brush, and the paper placed in a jar beside a bottle of chlorine (fig. 176), it will be found, on removing the stopper, that white characters soon make their appearance on the red ground.

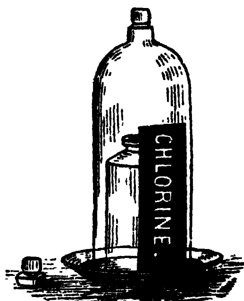


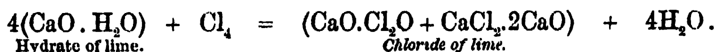
Fig. 176.

If a collection of coloured linen or cotton fabrics, or of artificial flowers, be exposed to the action of moist chlorine gas or of chlorine water, those which are dyed with organic colouring matters will be bleached at once, whilst the mineral colours will for the most part remain unaltered. Green leaves, immersed in chlorine, acquire a rich autumnal brown tint, and are eventually bleached. All flowers are very readily bleached by this gas.

Chlorine is very extensively employed for bleaching linen and cotton, the gas acting upon the colouring matter without affecting the fibre, but silk and wool present much less resistance to chemical action, and would be much injured by chlorine, so that they are always bleached by sulphurous acid.

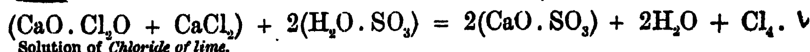
Neither chlorine itself nor its solution in water can be very conveniently employed for bleaching on the large scale, on account of the irritating effect of the gas, so that it is usual to employ it in the form of *chloride of lime*, from which it can be easily liberated as it is wanted.

104. *Chloride of lime* or *bleaching powder* is prepared by passing chlorine gas into boxes of lead or stone in which a quantity of slaked lime is spread out upon shelves. The lime absorbs nearly half its weight of chlorine, and forms a white powder which has a very peculiar smell, somewhat different from that of chlorine. The chloride of lime thus produced appears to consist of a mixture of *hypochlorite of lime* ($CaO.Cl_2O$) with *oxychloride of calcium* ($CaCl_2.2CaO$), the action of chlorine upon hydrate of lime being represented by the following equation:—



$$\underset{\text{Hydrate of lime.}}{4(CaO.H_2O)} + Cl_4 = \underset{\textit{Chloride of lime.}}{(CaO.Cl_2O + CaCl_2.2CaO)} + 4H_2O.$$

When the chloride of lime is treated with water, the hypochlorite of lime ($CaO.Cl_2O$) and chloride of calcium ($CaCl_2$) are dissolved, whilst hydrate of lime is left. If this solution be added to blue litmus, it will be found to exert little bleaching action, but on adding a little acid (sulphuric, for example), the blue colour will be discharged, the acid setting free the chlorine, which acts upon the colouring matter.



$$\underset{\text{Solution of \textit{Chloride of lime.}}}{(CaO.Cl_2O + CaCl_2)} + 2(H_2O.SO_3) = 2(CaO.SO_3) + 2H_2O + Cl_4.$$

Even carbonic acid will develope the bleaching property of chloride of lime, so that the above mixture may be decolorised by breathing into it through a glass tube.

When chloride of lime is used for bleaching on the large scale, the stuff to be bleached is first thoroughly cleansed from any grease or *weaver's dressing*, by boiling it in lime-water and in a weak solution of soda, and is then

immersed in a weak solution of the chloride of lime. This by itself, however, exerts very little action upon the natural colouring matter of the fibre, and the stuff is therefore next immersed in very dilute sulphuric acid, when the colouring matter is so far altered as to become soluble in the alkaline solution in which it is next immersed, and a repetition of these processes, followed up by a thorough rinsing, generally perfects the bleaching.

The property possessed by acids of liberating chlorine from the chloride of lime is applied in calico-printing to the production of white patterns upon a red ground. The stuff having been dyed with Turkey red, the pattern is imprinted upon it with a *discharge* consisting of an acid (tartaric, phosphoric, or arsenic) thickened with gum. On passing the fabric through a bath of weak chloride of lime, the colour is discharged only at those parts to which the acid has been applied, and where, consequently, chlorine is liberated.

The explanation above given of the bleaching effect of chlorine may probably be applied also to its so-called *disinfecting* properties. The atmosphere, in particular localities, is occasionally contaminated with poisonous substances, some of which are known only by their injurious effects upon the health, their quantity being so small that they do not appear in the results of the analysis of such air. Since, however, these substances appear to be acted upon by the same agents which are usually found to decompose organic compounds, they are commonly believed to be bodies of this class, and chlorine has been very commonly employed to combat these insidious enemies to health, since Guyton de Morveau, in the latter part of the last century, made use of it to destroy the odour arising from the bodies interred in the vaults beneath the cathedral of Dijon.

Among the offensive and unhealthy products of putrefaction of animal and vegetable matter, sulphuretted hydrogen, ammonia, and bodies similarly constituted, are found. That chlorine breaks up these hydrogen compounds is well known, and hence its great value for removing the unwholesome properties of the air in badly drained houses, &c.

Chloride of lime is one of the most convenient forms in which to apply chlorine for the purposes of fumigating and disinfecting. If a cloth saturated with the solution be suspended in the air, the carbonic acid in the latter causes a slow evolution of hypochlorous acid, which is even a more powerful disinfectant than chlorine itself. In extreme cases, where a rapid evolution of chlorine is required, the bleaching powder is placed in a plate, and diluted sulphuric acid is poured over it, or the powder may be mixed with half its weight of powdered alum in a plate, when a pretty rapid and regular escape of chlorine will ensue.

105. The discovery of chlorine and the discussions which ensued with respect to its real nature, contributed very largely to the advancement of chemical science. About the year 1770, the Swedish chemist Scheele (who afterwards discovered oxygen), first obtained chlorine by heating manganese ore with muriatic acid.

The construction which Scheele put upon the result of this experiment was one which was consistent with the chemistry of that date. He supposed the muriatic acid to have been deprived of *phlogiston*, and hence chlorine was termed by him *dephlogisticated muriatic acid*. This phlogiston had long been a subject of contention among philosophers, having

been originally assumed to exist in combination with all combustible bodies, and to be separated from them during their combustion. Towards the decline of the phlogistic theory, attempts were made to prove the identity of this imaginary substance with hydrogen, which shows how very nearly Scheele's reasoning approached to the truth, even with the very imperfect light which he then possessed. Berthollet's movement was retrograde when, ten years afterwards, he styled chlorine *oxygenised muriatic* or *oxymuriatic acid*, but the experiments of Gay-Lussac and Thénard, and more particularly those of Davy in 1811, proved decisively that hydrochloric acid was composed of chlorine and hydrogen, and that the effect of the black oxide of manganese in Scheele's experiment was to remove the hydrogen in the form of water, thus setting the chlorine at liberty.

Hydrochloric Acid.

HCl = 36·5 parts by weight = 2 vols.

106. This acid is found in nature among the gases emanating from active volcanoes, and occasionally in the spring and river waters of volcanic districts. For use it is always prepared artificially by the action of sulphuric acid upon common salt—



$$\underset{\text{Common salt.}}{2NaCl} + H_2O.SO_3 = 2HCl + \underset{\text{Sulphate of soda.}}{Na_2O.SO_3}$$

the sodium of the common salt changing places with the hydrogen of the sulphuric acid.

300 grains of common salt (previously dried in an oven) are introduced into a dry Florence flask (fig. 177), to which has been fitted, by means of a perforated cork, a tube bent twice at right angles to allow the gas to be collected by downward displacement. Six fluid drachms of strong sulphuric acid are poured upon the salt, and the cork having been inserted, the flask is very gently heated in order to promote the disengagement of the hydrochloric acid gas, which is collected in a perfectly dry bottle, the mouth of which, when full, may be covered with a glass plate smeared with a little grease. While being filled, the bottle may be closed with a perforated card.

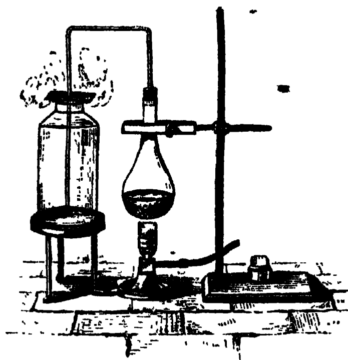


Fig. 177.—Preparation of hydrochloric acid gas.

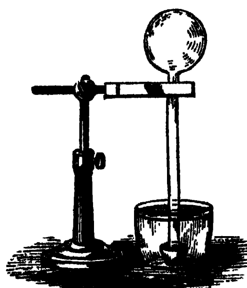
Common salt in powder sometimes froths to a very inconvenient extent with sulphuric acid; it is therefore often preferable to employ fragments of fused salt, prepared by fusing the common salt in a clay crucible, and pouring on to a clean dry stone.

A more regular supply of hydrochloric acid gas is obtained from 1½ oz. of sal-ammoniac in lumps, and 1¼ oz. (measured) of sulphuric acid.

The bottle will be known to be filled with gas by the abundant escape of the dense fumes which hydrochloric acid gas, itself transparent, produces by condensing the moisture of the air; for since the gas is much heavier than air (sp. gr. 1·247), it will not escape in any quantity from

the bottle until the latter is full. The odour of the gas is very suffocating, but not nearly so irritating as that of chlorine.

The powerful attraction for water is one of the most important properties of hydrochloric acid gas.

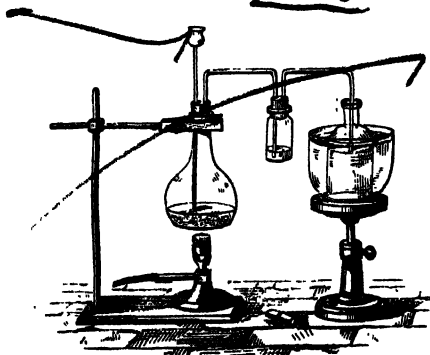

Fig. 178.

If a jar of hydrochloric acid gas be closed with a glass plate and inverted under water, it will be found, on removing the plate, that the gas is absorbed with great rapidity, the water being forced up into the bottle by the pressure of the external air in proportion as the gas is absorbed.

A Florence flask is more convenient than a gas bottle for this experiment. It must be perfectly dry, and thoroughly well filled with the gas, which may be allowed to escape abundantly from the mouth. The tube delivering the hydrochloric acid gas must be slowly withdrawn, so that the vacancy may be filled by gas and not by air. The flask is then closed with the thumb, and opened under water, which will enter it with great violence. The experiment may also be made as in the case of ammonia (fig. 178, see page 121).

The liquid hydrochloric, or *muriatic acid* of commerce, is a solution of the gas in water, and may be recognised by the grey fumes, with the peculiar odour of the acid, which it evolves when exposed to the air. One pint of water at a temperature of 40° F. is capable of absorbing 480 pints of hydrochloric acid gas, forming 1⅓ pint of the solution, having the specific gravity 1·21. The strength of the acid purchased in commerce is usually inferred from the specific gravity, by reference to tables indicating the weight of hydrochloric acid contained in solutions of different specific gravities. The strongest hydrochloric acid (sp. gr. 1·21) contains 43 per cent. by weight of the gas. The common acid has usually a bright yellow colour, due to the accidental presence of a little perchloride of iron (Fe_2Cl_6), and not unfrequently smells of chlorine.

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid in order to convert it into sulphate of soda, as a preliminary step to the production of carbonate of soda. The alkali manufacturer is compelled to condense the gas, for it is found to wither up the vegetation in the neighbourhood. For this purpose the hydrochloric acid gas is drawn up from the furnace through vertical cylinders filled with coke, over which streams of water are made to trickle. The water absorbs the acid, and is drawn off from below.


Fig. 179.—Preparation of solution of hydrochloric acid.

In preparing a pure solution of the acid for chemical use on a small scale, the gas prepared as above may be passed into a small bottle containing a very little water to wash the gas, or remove any sulphate of soda which may splash over, and then into a bottle about two-thirds filled with distilled water, the tube delivering the gas passing only about $\frac{1}{16}$ inch below the surface, so that the heavy solution of hydrochloric acid may fall to the bottom, and fresh water may be presented to the gas (fig. 179). For ordinary use, an acid of suitable strength is obtained by passing the gas from 6

ounces of common salt and 10 ounces of sulphuric acid into 7 (measured) ounces of water until its bulk has increased to 8 ounces. The bottle containing the water should be surrounded with cold water, since the absorption of hydrochloric acid by water is attended with evolution of heat.

When the concentrated solution of hydrochloric acid is heated in a retort, it evolves abundance of hydrochloric acid gas, rendering it probable that it is not a true chemical compound of water with the acid. The evolution of gas ceases when the remaining liquid contains 20 per cent. of acid (and has a sp. gr. of 1·10). If a weaker acid than this be heated, it loses water until it has attained this strength, when it distils unchanged.*

The concentrated solution forms a very convenient source from which to procure the gas. It may be heated in a flask, and the gas dried by passing through a bottle filled with fragments of pumice-stone wetted with concentrated sulphuric acid, being collected over the mercurial trough (fig. 180).

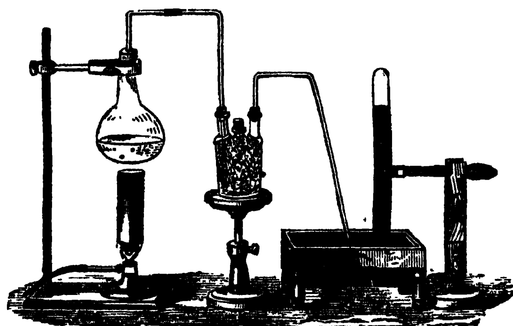


Fig. 180.

The avidity with which water absorbs hydrochloric acid is the more remarkable, because this gas can be liquefied only under a very high pressure, amounting at the ordinary temperature to about 40 atmospheres.

The liquefied hydrochloric acid has comparatively little action even upon those metals which decompose its aqueous solution with great violence; quick-lime is unaffected by it, and solid litmus dissolves in it with a faint purple colour, instead of the bright red imparted by the aqueous hydrochloric acid. Dry hydrochloric acid gas is not absorbed by carbonate of lime. (These facts answer the objection that anhydrous sulphuric acid (SO_3) cannot be considered an acid, because it has none of the powerful acid characters of oil of vitriol, since it cannot be doubted that hydrochloric acid is, in a chemical sense, an acid in its anhydrous state, though it manifests its acid properties only when water is present.)

The injurious action of hydrochloric acid gas upon growing plants is probably connected with its attraction for water. If a spray of fresh leaves is placed in a bottle of hydrochloric acid, it becomes at once brown and shrivelled.

107. *Action of hydrochloric acid upon metals.*—Those metals which have the strongest attraction for oxygen will also generally have the strongest attraction for chlorine, so that in respect to their capability of decomposing hydrochloric acid, they may be ranked in pretty nearly the

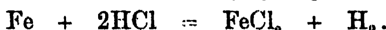
* The proportion of acid thus retained by the water varies directly with the atmospheric pressure to which it is exposed during the distillation.

same order as in their action upon water (p. 10). Since, however, the attraction of chlorine for the metals is generally superior to that of oxygen, the metals are more easily acted upon by hydrochloric acid than by water, the metal taking the place of the hydrogen, and a chloride of the metal being formed.

Even silver, which does not decompose water at any temperature, is dissolved, though very slowly, by boiling concentrated hydrochloric acid, the chloride of silver formed being soluble in the strong acid, though it may be precipitated by adding water.

Gold and platinum, however, are not attacked by hydrochloric acid, but if a little free chlorine be present, it converts them into chlorides.

Iron and zinc decompose the acid very rapidly in the cold, forming chlorides of iron and zinc, and liberating hydrogen—



$$Fe + 2HCl = FeCl_2 + H_2.$$

When potassium or sodium is exposed to hydrochloric acid gas, it immediately becomes coated with a white crust of chloride, which partly protects the metal from the action of the gas, but when these metals are heated to fusion in hydrochloric acid gas, they burn vividly—



$$Na + HCl = NaCl + H.$$

The composition of hydrochloric acid may be exhibited by confining a measured volume of the gas over mercury (see fig. 83, page 80), and passing up a freshly cut pellet of sodium. On gently agitating the tube, the gas diminishes in volume, and after a time will have contracted to one-half, and will be found to have all the properties of hydrogen. This result confirms that obtained by synthesis, as described above, that two volumes of hydrochloric acid contain one volume of hydrogen and one volume of chlorine.

The electrolysis of hydrochloric acid is exhibited in the V-tube represented in fig. 181, where the platinum plate *p* in the closed limb *o* is connected with a platinum wire sealed into the glass; the other limb, *h*, is open. If the closed limb be entirely filled with strong hydrochloric acid, and connected with the negative pole of a battery composed of five or six Grove's or Bunsen's cells, the positive pole being connected with *h*, hydrogen will rapidly collect in the closed limb, whilst the odour of chlorine will be perceived in the open limb. As soon as the liquid fills the open limb, the wire *h* is withdrawn, this limb closed with the thumb, and the hydrogen transferred to it by inclining the tube. After testing the hydrogen with a match, the poles of the battery may be reversed, when the chlorine will collect as gas in the closed limb as soon as the hydrochloric acid has become saturated with it.

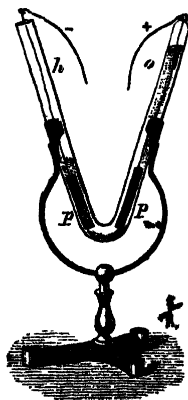


Fig. 181.

108.—*Action of hydrochloric acid upon metallic oxides.*—As a general rule it may be stated, that when hydrochloric acid acts upon the oxide of a metal, the results are water and a chloride of the metal, in which each atom of oxygen in the oxide has been displaced by two atoms of chlorine.

Thus, oxide of silver acted on by hydrochloric acid gives water and chloride of silver; $Ag_2O + 2HCl = H_2O + 2AgCl$.

Suboxide of copper (cuprous oxide) yields water and subchloride of copper (cuprous chloride); $Cu_2O + 2HCl = H_2O + Cu_2Cl_2$.

Sesquioxide of iron gives water and perchloride (sesquichloride) of iron; $Fe_2O_3 + 6HCl = 3H_2O + Fe_2Cl_6$.

With binoxide of tin, water and tetrachloride (bichloride) of tin are obtained; $SnO_2 + 4HCl = 2H_2O + SnCl_4$.

Oxide of antimony is converted into water and terchloride of antimony;



$$Sb_2O_3 + 6HCl = 3H_2O + 2SbCl_3.$$

In cases where the corresponding chloride does not exist, or is not stable under the conditions of the experiment, a chloride is formed containing less chlorine than is equivalent to the oxygen in the oxide, and the balance is evolved in the free state. Thus, when sesquioxide and binoxide of manganese are heated with hydrochloric acid—



$$Mn_2O_3 + 6HCl = 3H_2O + 2MnCl_2 + Cl_2$$



$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$$

Chromic acid, a chloride corresponding to which is not known to exist, when heated with hydrochloric acid, yields chromic chloride and chlorine; $2CrO_3 + 12HCl = 6H_2O + Cr_2Cl_6 + Cl_6$.

Every metallic oxide containing one atom of oxygen has a corresponding chloride of a stable character, but the higher oxides less frequently form corresponding chlorides endowed with any stability.

109. *Molecular weight of hydrochloric acid.*—It is ascertained by experiment that 36·5 grains of hydrochloric acid are required to neutralise one molecule (56 grains) of caustic potash. The number 36·5, therefore, represents the molecular weight of hydrochloric acid, and this receives confirmation from the circumstance that 36·5 parts by weight of hydrochloric acid gas occupy twice the volume of 1 part by weight of hydrogen (see page 36).

110. *Types of atomic formulæ; atomicity.*—On examining the composition by volume of hydrochloric acid, water, ammonia, and marsh-gas, it is seen that equal volumes of these compounds, measured in the gaseous state at the same temperature and pressure, contain respectively, 1, 2, 3, and 4 volumes of hydrogen.

Thus 2 volumes of hydrochloric acid gas contain 1 volume of chlorine and 1 volume of hydrogen.
- 2 volumes of watery vapour contain 1 volume of oxygen and 2 volumes of hydrogen.
- 2 volumes of ammonia contain 1 volume of nitrogen and 3 volumes of hydrogen.
- 2 volumes of marsh-gas contain 1 volume (?) of imaginary carbon vapour and 4 volumes of hydrogen.

In the case of the marsh-gas, it has been already explained that the volume occupied by a given weight of carbon vapour cannot be ascertained by experiment, but there are reasons to justify the assumption that 12 parts by weight of carbon vapour would occupy the same volume as 1 part by weight of hydrogen. In the other cases, the above statements exhibit the direct results of experiments previously described.

If it be allowed that one atom of each element occupies one volume, then hydrochloric acid, water, ammonia, and marsh-gas will contain, for one atom of chlorine, oxygen, nitrogen, and carbon, respectively, 1, 2, 3, and 4 atoms of hydrogen, or, taking the symbol for each element to represent one atom—

			Vols. H = 1	Weights. H = 1
Hydrochloric acid	= ClH	= HCl	= 2	= 36·5
Water	= O HH	= H_2O	= 2	= 18
Ammonia	= N HHH	= H_3N	= 2	= 17
Marsh-gas	= C HHHH	= H_4C	= 2	= 16

Since, on the atomic theory, hydrogen is accepted as the unit of atomic weight and volume, it appears reasonable to fix upon it as representing the unit of combining power, and to classify the elements according to the tendency of their atoms to imitate the combining power of one or more atoms of hydrogen.

By the *atomicity* or *quantivalence* of an element is meant the number expressing the hydrogen-atoms to which one atom (or volume) of that element is usually equivalent.

Thus, the atomicity of chlorine is = 1, for one volume (or atom) of this element not only combines with, and neutralises the properties of, one atom (or volume) of hydrogen, but is capable of representing, or occupying the place of, one atom of hydrogen in its compounds (see page 150).

The atomicity of oxygen is = 2, since one volume (or atom) of oxygen combines with, and neutralises, two atoms (or volumes) of hydrogen in water, and is generally capable of occupying the place of two atoms of hydrogen in the compounds of that element.

The atomicity of nitrogen is = 3, for one volume (or atom) of nitrogen neutralises the properties of three atoms (or volumes) of hydrogen in ammonia, and is often found to occupy the place of three atoms of hydrogen in its compounds.

The atomicity of carbon is = 4, for one volume (or atom) of *imaginary* carbon vapour is combined, in marsh-gas, with four atoms (or volumes) of hydrogen, and in its compounds with other elements, one atom of carbon is usually found representing four atoms of hydrogen.

Since hydrochloric acid, water, ammonia, and marsh-gas are the most conspicuous members of large classes of chemical compounds, they are often referred to as *types*, and the elements, chlorine, oxygen, nitrogen, and carbon, are taken as the representatives of the various classes into which the elements are divided according to their atomicities.

Chlorine is the type of one-atom elements (technically called *monatomic, uni-equivalent, monad* elements), the atomic weights of which are represented by the same numbers as their equivalent weights.

Oxygen is the type of two-atom elements (*di-atomic, bi-equivalent, dyad* elements), of which the number representing the equivalent weight is half of that which represents the atomic weight.

Equivalent of oxygen = 8.
Atom of oxygen = 16.

Nitrogen is the type of three-atom elements (*tri-atomic, ter-equivalent, triad* elements), of which the number representing the equivalent weight is commonly taken as identical with that which represents the atomic weight, though if the equivalentic system were rigorously carried out, the equivalent should be one-third of the atomic weight.

Carbon is the type of four-atom elements (*tetratomic, quadrequivalent, tetrad* elements), of which the number representing the equivalent weight

ought to be one-fourth of that which expresses the atomic weight, whereas it is usually represented as half that number.

Equivalent of carbon = 6.
Atom of carbon = 12.

Such anomalies as these are unavoidable during the present transitional period through which chemistry appears to be passing towards the ultimate adoption of atomic (or molecular) formulæ in the place of equivalent formulæ, a change which offers dazzling prospects of advantage in speculative chemistry, but will probably be of less service in practice than the preservation of equivalent formulæ, so corrected as to remove the anomalies presented in some few cases.

The experience of the last few years seems to warrant the belief that it will be long before experiment (the only possible final resort for the chemist) has so far removed the exceptions to the atomic formulæ which are presented, in some cases, by the gaseous volumes and specific heats of the elements, that these formulæ can be said to present us with so true a record of the actual results of experiment as to console us for the loss of the greater simplicity and practical utility of the equivalent formulæ.

It is remarkable that the four elements, hydrogen, oxygen, nitrogen, and carbon, which compose the chief part of living matter, are respectively monatomic, diatomic, triatomic, and tetratomic elements.

In speculations relating to the atomic structure of compounds, it is now usual to represent graphically the atomicity of each element; thus a monatomic element, like hydrogen, is represented as affording one point of attachment, which may be indicated by writing the symbol H—; a diatomic element, like oxygen, affords two points of attachment, as shown by writing its atomic symbol —O—; accordingly, to form water, the diatomic oxygen attaches to itself two atoms of hydrogen, as represented by the molecular formula H—O—H, whereas in the peroxide of hydrogen (H_2O_2) the second atom of oxygen is only held by one point of attachment, so that the graphic expression H—O—H—O— accounts at once for its tendency to decompose into water and free oxygen. A triatomic element, such as nitrogen, has three points of attachment >N—, and thus in ammonia, attaches to itself three atoms of hydrogen H, H >N—H. The tetratomic element, carbon, affords four points of attachment >C< and thus marsh-gas (CH_4) is represented by H, H >C< H, H, and carbonic acid (CO_2) by O<>C<>O.

Compounds of Chlorine with Oxygen.

111. It is worthy of notice that whilst chlorine and hydrogen so readily unite, there is no method by which chlorine can be made to combine in a direct manner with oxygen, all the compounds of these elements having been hitherto obtained only by indirect processes. An excellent illustration is thus afforded of the fact, that the more closely substances resemble each other in their chemical relations, the less will be their tendency to

combine, for chlorine and oxygen are both highly electronegative bodies, and therefore, having both a powerful attraction for the electropositive hydrogen, their attraction for each other is of a very low order.

112. *Hypochlorous acid* (Cl_2O) is of some practical interest as one of the constituents of *chloride of lime, chloride of soda*, and other bleaching compounds. It is prepared by passing dry chlorine gas over dry precipitated oxide of mercury, and condensing the product in a tube surrounded with a mixture of ice and salt—



$$HgO \text{ (oxide of mercury)} + Cl_4 = HgCl_2 \text{ (bichloride of mercury)} + Cl_2O.$$

The hypochlorous acid is thus obtained as a deep red liquid, which boils at 19° F., evolving a yellow vapour thrice as heavy as air, and having a very powerful and peculiar odour. This vapour is remarkably explosive, the heat of the hand having been known to cause its separation into its constituents, when two volumes of the vapour yield two volumes of chlorine and one volume of oxygen. As might be expected, most substances which have any attraction for oxygen or chlorine will decompose the gas, sometimes with explosive violence. Even hydrochloric acid decomposes it; one volume of hypochlorous acid gas is entirely decomposed by two volumes of hydrochloric acid, yielding water and chlorine—



$$Cl_2O + 2HCl = H_2O + Cl_4.$$

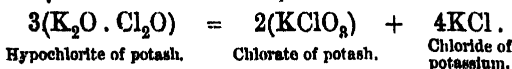
Hypochlorous acid is a powerful bleaching agent, both its chlorine and oxygen acting upon the colouring matter in the manner explained at page 150.

Hypochlorous acid is absorbed in large quantity by water. The solution may be very readily prepared by shaking the red oxide of mercury with water in a bottle of chlorine as long as the gas is absorbed. The greater part of the chloride of mercury which is produced combines with the excess of oxide of mercury to form a brown insoluble oxychloride, whilst the hypochlorous acid and a little chloride of mercury remain in solution. This solution is a most powerful oxidising and bleaching agent; it erases writing ink immediately, and does not corrode the paper if it be carefully washed. Printing ink, which contains lamp-black and grease, is not bleached by hypochlorous acid, so that this solution is very useful for removing ink stains from books, engravings, &c.

The action of some metals and their oxides upon solution of hypochlorous acid is instructive. Iron seizes upon the oxygen, whilst the chlorine is liberated; copper takes both the oxygen and chlorine, whilst silver combines with the chlorine and liberates oxygen. Oxide of lead (PbO) removes the oxygen, becoming peroxide of lead (PbO_2), and liberating chlorine, but oxide of silver converts the chlorine into chloride of silver, and liberates the oxygen; $Ag_2O + Cl_2O = 2AgCl + O_2$.

The salts of hypochlorous acid, or *hypochlorites*, are not known in a pure state, but are obtained in solution by neutralising the solution of hypochlorous acid with bases. They are decomposed even by carbonic acid, with liberation of hypochlorous acid.

When the solution of a hypochlorite is boiled, it becomes converted into a mixture of chloride and chlorate; thus—



$$3(K_2O \cdot Cl_2O) = 2(KClO_3) + 4KCl.$$

Hypochlorite of potash. Chlorate of potash. Chloride of potassium.

This change is turned to practical account in the manufacture of chlorate of potash. It is much hindered by the presence of an excess of alkali. The solution of hypochlorous acid itself, when exposed to light, is decomposed into chloric acid and free chlorine—



$$5Cl_2O + H_2O = 2HClO_3 + Cl_8.$$

Chloride of lime (see p. 151) is the most important compound containing hypochlorous acid. Its formula has already been given as $CaO.Cl_2O + CaCl_2.2CaO + 4Aq$, showing it to be a mixture of hypochlorite of lime with oxychloride of calcium. When this compound is distilled with a small quantity of diluted sulphuric acid, a solution of hypochlorous acid is obtained; but if an excess of acid be used, the chloride of calcium is decomposed, furnishing hydrochloric acid, which acts upon the hypochlorous acid, and free chlorine is the result. Alcohol, although capable of dissolving chloride of calcium, does not extract that salt from bleaching powder, because it is combined with lime; but an excess of water decomposes the compound of chloride of calcium with lime, and dissolves the former.

Bleaching powder is liable to decomposition when kept, its hypochlorite of lime evolving oxygen, and becoming converted into chloride of calcium, which attracts moisture greedily, and renders the bleaching powder deliquescent. It has been known to shatter the glass bottle in which it was preserved, in consequence of the accumulation of oxygen.

When a solution of salt of manganese or cobalt is added to solution of chloride of lime, a black precipitate of binoxide of manganese or sesquioxide of cobalt is obtained, the oxide of manganese or of cobalt acquiring additional oxygen from the hypochlorite of lime, and forming an oxide which is indifferent, and does not remain in combination with the acid. If this precipitate be boiled with an excess of solution of chloride of lime, it causes a rapid disengagement of oxygen in some manner that has not yet been clearly explained.

Large quantities of oxygen are easily obtained by adding a few drops of solution of nitrate of cobalt to solution of chloride of lime, and applying a gentle heat.

Hypochlorite of soda, which is very useful for removing ink, is prepared in solution by decomposing solution of chloride of lime with solution of carbonate of soda, and separating the carbonate of lime by filtration. The solution is generally called "chloride of soda."

113. *Chloric acid* ($HClO_3$).—This acid is appropriately studied here, since its compounds are usually obtained by the decomposition of the hypochlorites. The only compound of chloric acid which possesses any great practical importance is the chlorate of potash ($KClO_3$) which is largely employed as a source of oxygen, as an ingredient of several explosive compositions, and in the manufacture of lucifer matches.

Chlorate of potash.—The simplest method of obtaining this salt consists in passing an excess of chlorine rapidly into a strong solution of potash, when the liquid becomes hot enough to decompose the hypochlorite of potash first formed, into chloride of potassium, which remains in solution, and chlorate of potash, which is deposited in tabular crystals, the ultimate result being expressed by the equation—



$$6(KHO) + Cl_6 = KClO_3 + 5KCl + 3H_2O.$$

If carbonate of potash or a weak solution of hydrate of potash be employed, the liquid will require boiling after saturation with chlorine, in order to convert the hypochlorite into chlorate.

The following proportions will be found convenient for the preparation of chlorate of potash on the small scale as a laboratory experiment. 300 grains of carbonate of potash are dissolved, in a beaker, with two measured ounces of water. 600 grains of common salt are mixed with 450 grains of binoxide of manganese, and very gently heated in a flask (fig. 182) with a mixture of 1½ ounce (measured) of strong sulphuric acid and 4 ounces (measured) of water, the evolved chlorine being passed through a rather wide bent tube into the solution of carbonate of potash.

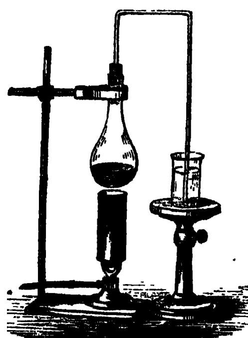
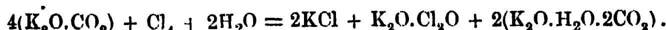


Fig. 182.

At first no action will appear to take place, although the solution absorbs the chlorine; because the first portion of that gas converts the carbonate of potash into a mixture of hypochlorite of potash, chloride of potassium, and bicarbonate of potash, some crystals of which will probably be deposited—



$$4(K_2O.CO_2) + Cl_4 + 2H_2O = 2KCl + K_2O.Cl_2O + 2(K_2O.H_2O.2CO_2).$$

On continuing to pass chlorine, these crystals will redissolve, and brisk effervescence will be caused by the expulsion of the carbonic acid from the bicarbonate of potash—



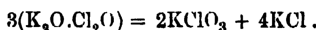
$$2(K_2O.H_2O.2CO_2) + Cl_4 = 2KCl + K_2O.Cl_2O + 2H_2O + 4CO_2.$$

When this effervescence has ceased, and the chlorine is no longer absorbed by the liquid, the change is complete, the ultimate result being represented by the equation—



$$2(K_2O.CO_2) + Cl_4 = 2KCl + K_2O.Cl_2O + 2CO_2.$$

The solution (which often has a pink colour, due to a little permanganate of potash) is now poured into a dish, boiled for two or three minutes, filtered, if necessary, from any impurities (silica, &c.,) derived from the carbonate of potash, and set aside to crystallise. The ebullition has converted the hypochlorite of potash into chlorate of potash and chloride of potassium—

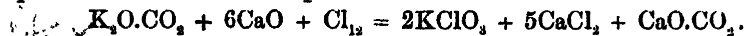


$$3(K_2O.Cl_2O) = 2KClO_3 + 4KCl.$$

The latter being soluble in about three times its weight of cold water, is retained in the solution, whilst the chlorate of potash, which would require about sixteen times its weight of cold water to hold it dissolved, is deposited in brilliant rhomboidal tables. These crystals may be collected on a filter, and purified from the adhering solution of chloride of potassium by pressure between successive portions of filter-paper. If they be free from chloride of potassium, their solution in water will not be changed by nitrate of silver, which would yield a milky precipitate of chloride of silver if that impurity were present. Should this be the case, the crystals must be redissolved in a small quantity of boiling water and recrystallised.

The above processes for preparing the chlorate of potash are far from economical, since five-sixths of the potash are converted into chloride, being employed merely to furnish oxygen to convert the chlorine into chloric acid. In manufacturing chlorate of potash upon the large scale, a much cheaper material, lime, is used to furnish the oxygen, one molecule of carbonate of potash being mixed with six molecules of slaked lime, and the damp mixture saturated with chlorine. On treating the mass with boiling water, a solution is obtained which contains chlorate of potash and chloride of calcium, the latter, being very soluble, remains in the liquor from which the chlorate of potash crystallises on cooling. The

ultimate result of the action of chlorine upon the mixture of carbonate of potash and lime is thus expressed—



$$K_2O.CO_2 + 6CaO + Cl_{12} = 2KClO_3 + 5CaCl_2 + CaO.CO_2.$$

A still cheaper salt of potassium, the chloride, has recently been employed with great economy as a substitute for the carbonate of potash. The solution of chloride of potassium is mixed with lime, and saturated with chlorine in close leaden tanks. The solution is filtered, evaporated nearly to dryness, and redissolved in hot water, when the chlorate of potash crystallises out on cooling. The chloride of calcium is precipitated by carbonate of soda to obtain *precipitated chalk.*

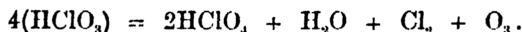
Anhydrous chloric acid (Cl_2O_5) has never been obtained in the separate state; but its hydrate ($H_2O.Cl_2O_5$ or $HClO_3$) may be procured by decomposing a solution of chlorate of potash with hydrofluosilicic acid, when the potassium is deposited as an insoluble silico-fluoride, and hydrated chloric acid is found in the solution*—



$$2KClO_3 + 2HF.SiF_4 \text{ (Hydrofluosilicic acid)} = 2HClO_3 + 2KF.SiF_4.$$

On evaporating the solution at a temperature not exceeding 100° F., the hydrated chloric acid is obtained as a yellow liquid with a peculiar pungent smell.

In its chemical characters, hydrated chloric acid bears a very strong resemblance to hydrated nitric acid, but is far more easily decomposed. It cannot even be kept unchanged for any length of time, and at temperatures above 104° F. it is decomposed into perchloric acid, chlorine, and oxygen—



$$4(HClO_3) = 2HClO_4 + H_2O + Cl_2 + O_3.$$

Hydrated chloric acid is one of the most powerful oxidising agents; a drop of it will set fire to paper, and it oxidises phosphorus (even the amorphous variety) with explosive violence.

Chlorates.—Chloric acid, like nitric, is monobasic, containing only one atom of hydrogen replaceable by a metal. The chlorates resemble the nitrates in their oxidising power, but generally act at lower temperatures, in consequence of the greater facility with which the chlorates part with their oxygen.

A grain or two of chlorate of potash, rubbed in a mortar with a little sulphur, for example, detonates violently, evolving a powerful odour of chloride of sulphur. Chlorate of potash and sulphur were used in some of the first percussion caps, but being found to corrode the nipple of the gun, they gave place to the *anticorrosive caps* containing fulminate of mercury.

If a little powdered chlorate of potash be mixed, on a card, with some black sulphide of antimony, and wrapped up in paper, the mixture will detonate when struck with a hammer.

A mixture of this description is employed in the *friction tubes* used for firing cannon. These are small tubes (A, fig. 183) of sheet copper (for military) or of quill (for naval use), filled with gunpowder; in the upper part of the tube a small copper rasp (B) is tightly fixed across it, and on each side of the rasp a pellet is placed containing 12 parts of chlorate of potash, 12 of sulphide of antimony, and 1 of sulphur, these ingredients being worked up into a paste with a solution of an ounce of shellac in a pint of spirit of wine. The friction tube is fixed in the vent of the gun, and the copper rasp quickly withdrawn by a cord in the hands of the gunner, when the detonating pellets explode and fire the powder.

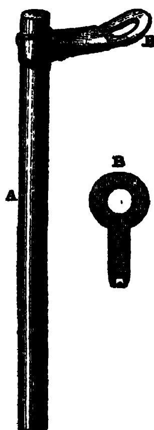


Fig. 183.

* 440 grain measures of hydrofluosilicic acid of sp. gr. 1078 will decompose 100 grains of chlorate of potash.

The earliest lucifer matches were tipped with a mixture of chlorate of potash, sulphide of antimony and starch, and were kindled by drawing them briskly through a doubled piece of sand-paper.

At high temperatures the chlorates act violently upon combustible bodies. A little chlorate of potash sprinkled upon red-hot coals causes a very violent deflagration. If a little chlorate of potash be melted in a deflagrating spoon, and plunged into a bottle or flask containing coal-gas (fig. 184), the salt burns with great brilliancy, its oxygen combining with the carbon and hydrogen in the gas, which becomes, in this case, the *supporter of combustion.* The flask may be conveniently filled with coal-gas by inverting it, and passing a flexible tube from the gas pipe up into it.

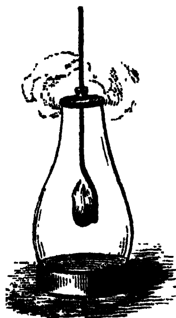


Fig. 184.

Chlorate of potash is much used in the manufacture of fireworks, especially as an ingredient of coloured fire compositions, which generally consist of chlorate of potash mixed with sulphur, and with some metallic compound to produce the desired colour in the flame. They are not generally made of the best quality on the small scale, from want of attention to the very finely powdered state of the ingredients, the absence of all moisture, and the most intimate mixture.

If these precautions be attended to, the following prescription will give very good coloured fires :—

Red fire.—40 grains of nitrate of strontia, thoroughly dried over a lamp, are mixed with 10 grains of chlorate of potash, and reduced to the finest possible powder. *In another mortar* 13 grains of sulphur are mixed with 4 grains of black sulphide of antimony (crude antimony). The two powders are then placed upon a sheet of paper, and very intimately mixed with a bone knife, avoiding any great pressure. A little heap of the mixture touched with a red-hot iron ought to burn with a uniform red flame, the colour being due to the strontium.

Blue fire.—15 grains of chlorate of potash are mixed with 10 grains of nitrate of potash and 30 grains of oxide of copper, in a mortar. The finely-powdered mixture is transferred to a sheet of paper, and mixed, by a bone knife, with 15 grains of sulphur. The colour of the fire is given chiefly by the copper.

Green fire.—10 grains of chlorate of baryta are mixed with 10 grains of nitrate of baryta in a mortar, and afterwards, on paper, with 12 grains of sulphur. The barium is the cause of the bright green colour of the flame.

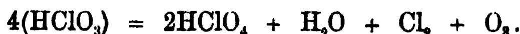
These compositions are rather dangerous to keep, since they are liable to spontaneous combustion.

White gunpowder is a mixture of two parts of chlorate of potash with one part of dried yellow prussiate of potash, and one part of sugar, which explodes very easily under friction or percussion.

The decomposition of chlorate of potash by heat into oxygen and chloride of potassium is attended with evolution of heat, unlike most cases of chemical decomposition, in which heat is generally absorbed. If chlorate of potash be heated to the point at which it begins to decompose, and a little peroxide of iron be thrown into it, enough heat will be evolved to bring the mass to a red heat, although the peroxide of iron is not oxidised. Experiment has shown that one part of chlorate of potash evolves, during decomposition, nearly 39 units of heat, or enough heat to raise 39 parts of water through 1° C. This anomalous evolution of heat must of course contribute to increase the energy of explosive mixtures containing the chlorate, and may be accounted for on the supposition, that the heat evolved by the combination of the potassium with the chlorine to form chloride of

potassium exceeds that which is absorbed in effecting the chemical disintegration of the chlorate.

114. Anhydrous *perchloric acid* (Cl_2O_7) is not known. The hydrated acid is obtained by evaporating down, at a boiling heat, the solution of chloric acid obtained by decomposing chlorate of potash with hydrofluosilicic acid (see p. 163), when the chloric acid is decomposed into perchloric acid, chlorine, and oxygen—



$$4(HClO_3) = 2HClO_4 + H_2O + Cl_2 + O_3.$$

When the greater part of the water has been boiled off, the liquid may be introduced into a retort and distilled. After the remainder of the water has passed over, it is followed by a heavy oily liquid which is $HClO_4.2H_2O$. If this be mixed with four times its volume of strong sulphuric acid and again distilled, the pure hydrated perchloric acid ($HClO_4$) first passes over as a yellow watery liquid. If the distillation be continued, the oily $HClO_4.2H_2O$ distils over, and if this be mixed with the former and cooled, it yields silky crystals containing $HClO_4.H_2O$, which are decomposed at 230° F. into $HClO_4$, which may be distilled off, and $HClO_4.2H_2O$, which is left in the retort—



$$2(HClO_4.H_2O) = HClO_4 + HClO_4.2H_2O.$$

The pure hydrated perchloric acid is a colourless, very heavy liquid (sp. gr. 1·782), which soon becomes yellow from decomposition. It cannot be kept for any length of time. When heated it undergoes decomposition, often with explosion. In its oxidising properties it is more powerful than chloric acid. It burns the skin in a very serious manner, and sets fire to paper, charcoal, &c., with explosive violence. This want of stability, however, belongs only to the pure hydrate. If water be added to it heat is evolved, and a diluted acid of far greater permanence is obtained. Diluted perchloric acid does not even bleach, but reddens litmus in the ordinary way.

Perchloric acid is monobasic. The *perchlorates* are decomposed by heat, evolving oxygen, and leaving chlorides; thus—



$$KClO_4 \text{ (Perchlorate of potash)} = KCl + O_4.$$

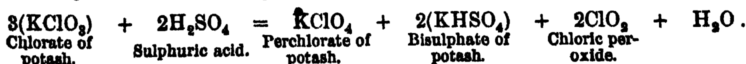
The perchlorate of potash is always formed in the first stage of the decomposition of chlorate of potash by heat—



$$2(KClO_3) = KClO_4 + KCl + O_2.$$

If a few crystals of chlorate of potash be heated in a test-tube, they first melt to a perfectly clear liquid, which soon evolves bubbles of oxygen. After a time the liquid becomes pasty, and if the contents of the tube, after cooling, be dissolved by boiling with water, the latter will deposit, as it cools, crystals of perchlorate of potash. These are readily distinguished from chlorate of potash by their not yielding a yellow gas (ClO_2) when treated with strong sulphuric acid. The perchlorate of potash is remarkable as one of the least soluble of the salts of potash, requiring 150 times its weight of cold water to dissolve it. Neither perchloric acid nor any of its salts is applied to any useful purpose.

115. *Chloric peroxide* or *peroxide of chlorine* (ClO_2) is dangerous to prepare and examine on account of its great instability and violently explosive character. It is obtained by the action of strong sulphuric acid upon chlorate of potash—



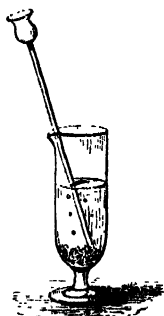
$$\underset{\text{Chlorate of potash.}}{3(KClO_3)} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Perchlorate of potash.}}{KClO_4} + \underset{\text{Bisulphate of potash.}}{2(KHSO_4)} + \underset{\text{Chloric peroxide.}}{2ClO_2} + H_2O.$$

It is a bright yellow gas, with a chlorous and somewhat aromatic smell, and sp. gr. 2·32; condensible at —4° F. to a red, very explosive liquid. The gas is gradually decomposed into its elements by exposure to light, and a temperature of 140° F.

causes it to decompose with violent explosion into a mixture of chlorine and oxygen, the volume of which is one-third greater than that of the compound.

On a small scale chloric peroxide may be prepared with safety by pouring a little strong sulphuric acid upon one or two crystals of chlorate of potash in a test-tube supported in a holder. The crystals at once acquire a red colour, which gradually diffuses itself through the liquid, and the bright yellow gas collects in the tube. If heat be applied, the gas will explode, and the colour and odour of chloric peroxide will be exchanged for those of chlorine. If the chlorate of potash employed in this experiment contains chloride of potassium, explosion often takes place in the cold, since the hydrochloric acid evolved by the action of the acid upon that salt decomposes a part of the chloric peroxide, and thus provokes the decomposition of the remainder.

Chloric peroxide is easily absorbed by water, and the solution has powerful bleaching properties. Combustible bodies, such as sulphur and phosphorus, decompose the gas, as might be expected, with great violence. This powerful oxidising action of chloric peroxide upon combustible substances, appears to be the cause of the property possessed by mixtures of such substances with chlorate of potash to inflame when touched with strong sulphuric acid.


Fig. 185.

If a few crystals of chlorate of potash be thrown into a glass of water (fig. 185), one or two small fragments of phosphorus dropped upon them, and some strong sulphuric acid poured down a funnel tube to the bottom of the glass, the chloric peroxide will inflame the phosphorus with bright flashes of light and slight detonations.

Powdered sugar, mixed with chlorate of potash, on paper, will burn brilliantly when touched with a glass rod dipped in strong sulphuric acid. Matches may be prepared which inflame when moistened with sulphuric acid, by dipping the ends of splinters of wood in melted sulphur, and when cool, tipping them with a mixture of 5 grains of sugar and 15 grs. of chlorate of potash made into a paste with 4 drops of water. When dry they may be fired by dipping them into a bottle containing asbestos moistened with strong sulphuric acid. These matches, under the names of Eupyrion and Vesta matches, were used before the introduction of phosphorus into general use. The Promethean light was an ornamental scented paper spill, one end of which contained a small glass bulb of sulphuric acid surrounded with a mixture of chlorate of potash and sugar, which inflamed when the end of the spill was struck or squeezed, so as to break the bulb containing the sulphuric acid. The paper was waxed in order to make it inflame more easily. Percussion fuses, &c., have been often constructed upon a similar principle.

Chloric peroxide used to be called hypochloric acid, but, like nitric peroxide, it appears to have no claim to be considered a true acid, since, in contact with the alkalies, it yields mixtures of chlorites and chlorates; thus—

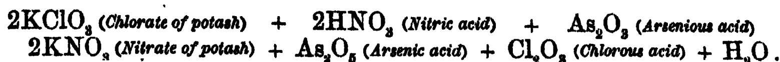


$$4ClO_2 + 2K_2O = K_2O.Cl_2O_3 + 2KClO_3.$$

Euchlorine, the deep yellow, dangerously explosive gas evolved by the action of strong hydrochloric acid upon chlorate of potash, appears to be a compound of anhydrous chloric and chlorous acids ($2Cl_2O_5.Cl_2O_3$) mixed with free chlorine.

116. *Chlorous acid* (Cl_2O_3)* is another unstable and dangerously explosive gas, obtained by the action of a very gentle heat upon a mixture of three parts of arsenious acid, four of chlorate of potash, and sixteen of diluted nitric acid (sp. gr. 1·24)—

* This gas occupies three times the volume of an atom of hydrogen, instead of twice that volume, as usual.



$$2KClO_3 \text{ (Chlorate of potash)} + 2HNO_3 \text{ (Nitric acid)} + As_2O_3 \text{ (Arsenious acid)}$$
$$2KNO_3 \text{ (Nitrate of potash)} + As_2O_5 \text{ (Arsenic acid)} + Cl_2O_3 \text{ (Chlorous acid)} + H_2O.$$

Chlorous acid is a deep yellowish green heavy gas (sp. gr. 2·65) which is absorbed by water, and decomposed even more easily than the chloric peroxide. It is a weak acid, its salts, the *chlorites*, being decomposed even by carbonic acid. A mixture of ice and salt does not liquefy chlorous acid, but an intense cold condenses it to a red liquid, of sp. gr. 1·33, which boils at a little above the melting-point of ice, and explodes at a somewhat higher temperature.

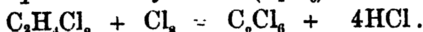
117. *General review of the oxides of chlorine.*—Several points of resemblance will have been noticed between the series of oxides of chlorine and those of nitrogen, but the former are much less stable than the latter. Chlorous acid (Cl_2O_3), like nitrous acid (N_2O_3), is a weak acid; chloric peroxide (ClO_2 or Cl_2O_4) is easily resolved by bases into chlorous and chloric acids, just as nitric peroxide (NO_2 or N_2O_4) is resolved into nitrous and nitric acids. The hydrated chloric acid ($HClO_3$) is a powerful oxidising agent like hydrated nitric acid (HNO_3), and the chlorates resemble the nitrates in their solubility in water and their oxidising power. The composition by volume of those oxides of chlorine which are known in the separate state, is exhibited in the following table:—

	Formula.	Molecular Weight.	Molecular Volume.	By Volume.	
				Cl	O
Hypochlorous acid .	Cl_2O	87	2	2	1
Chlorous acid . . .	Cl_2O_3	119	3	2	3
Chloric peroxide . .	ClO_2	67·5	2	1	2

Some chemists refuse to regard the hypochlorites and chlorites, as composed of basic oxides united with hypochlorous and chlorous acids respectively, but consider them as derived from (*hypothetical*) hydrated hypochlorous acid ($H_2O.Cl_2O$ or $HClO$) and (*hypothetical*) hydrated chlorous acid ($H_2O.Cl_2O_3$ or $HClO_2$), by the substitution of metals for the hydrogen contained in those compounds. Thus hypochlorite of lime ($CaO.Cl_2O$) would become $Ca(ClO)_2$, chlorite of potash ($K_2O.Cl_2O_3$) would be $KClO_2$.

Chlorides of Carbon.

118. It has already been seen that chlorine has no direct attraction for carbon, the two elements not being known to enter into direct combination, but several chlorides of carbon may be obtained by the action of chlorine upon other compounds of carbon. Thus, if Dutch liquid ($C_2H_4Cl_2$), produced by the combination of olefiant gas with chlorine (p. 92), be acted upon with an excess of chlorine in sunlight, the whole of its hydrogen is removed in the form of hydrochloric acid, and an equivalent amount of chlorine is substituted for it, yielding the *trichloride*, formerly called *sesquichloride of carbon* (C_2Cl_6)—



$$C_2H_4Cl_2 + Cl_8 = C_2Cl_6 + 4HCl.$$

Trichloride of carbon is a white crystalline solid, with an aromatic odour rather like that of camphor. It fuses at 320° F., and boils at 360°,

subliming unchanged. It is not dissolved by water, but is soluble in alcohol and ether.

When the vapour of trichloride of carbon is passed through a tube containing fragments of glass heated to redness, it is decomposed into chlorine and a colourless liquid, which is the dichloride, formerly called *protochloride of carbon* (C_2Cl_4). It has an aromatic odour, and boils at 248° F.; is heavier than water (sp. gr. 1·5), which does not dissolve it, and is soluble in alcohol and ether.

By passing the vapour of this dichloride of carbon through tubes heated to bright redness, it is decomposed into chlorine and monochloride, formerly called *subchloride of carbon* (C_2Cl_2), which forms silky crystals almost free from odour, insoluble in water, but soluble in ether, and capable of being sublimed unchanged at a high temperature. It burns in air with a red smoky flame.

Tetrachloride (*bichloride*) *of carbon* (CCl_4) has been mentioned (p. 150) as the final result of the action of chlorine upon marsh-gas (CH_4) and upon chloroform ($CHCl_3$). It is easily obtained in large quantity, by passing chlorine (dried by passing through a tube containing pumice wetted with strong sulphuric acid) (fig. 186) through a bottle containing bisulphide of

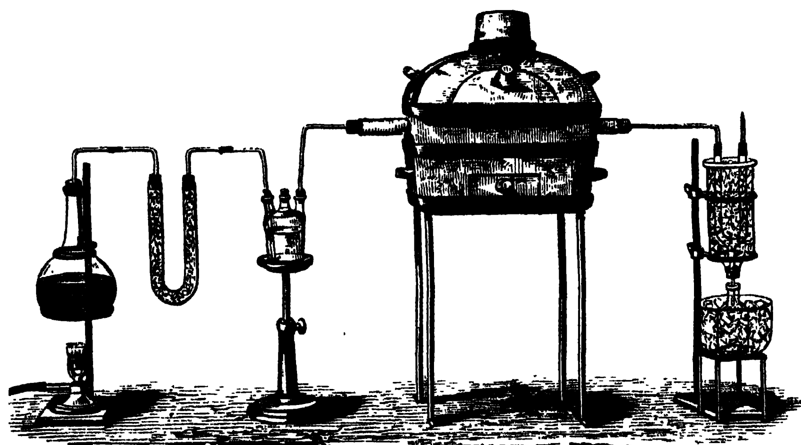
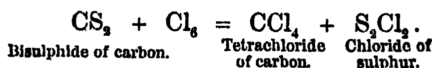


Fig. 186.—Preparation of bichloride of carbon.

carbon, and afterwards through a porcelain tube wrapped in sheet copper, and filled with fragments of broken porcelain, maintained at a red heat by a charcoal or gas furnace, and condensing the products in a bottle surrounded by ice. A mixture of tetrachloride of carbon and chloride of sulphur is thus obtained—



$$\underset{\text{Bisulphide of carbon.}}{CS_2} + Cl_6 = \underset{\text{Tetrachloride of carbon.}}{CCl_4} + \underset{\text{Chloride of sulphur.}}{S_2Cl_2}.$$

By shaking this mixture with solution of potash, the chloride of sulphur is decomposed and dissolved, whilst the tetrachloride of carbon separates and falls to the bottom. The upper layer having been poured off, the tetrachloride may be purified by distillation.

Tetrachloride of carbon is a colourless liquid much heavier than water (sp. gr. 1·6), having a peculiar odour, and boiling at 172° F. It may be solidified at − 9° F. The tetrachloride is insoluble in water, but dissolves in alcohol and ether.

By the action of chlorine on naphthaline ($C_{10}H_8$) Laurent obtained, as the ultimate result, a crystalline chloride of carbon containing $C_{10}Cl_8$, to which he gave the name *chlonaphthalise.*

It will be noticed that each of the compounds of chlorine with carbon, except the sesquichloride, has its parallel in the compounds of hydrogen with carbon;* thus—

Acetylene	C_2H_2	corresponds to	monochloride	of carbon	C_2Cl_2
Olefiant gas	C_2H_4	„	dichloride	„	C_2Cl_4
Marsh-gas	CH_4	„	tetrachloride	„	CCl_4

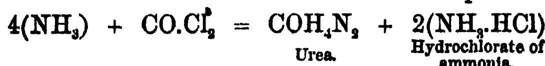
The history of trichloride of carbon affords an instructive instance of the influence of the molecular weight of a compound upon its properties. By passing the vapour of tetrachloride of carbon through a tube heated to dull redness, a liquid is obtained which is found by analysis to contain precisely the same proportions of carbon and chlorine as the solid trichloride above described, but the specific gravity of its vapour ($H=1$) is only 59·25, which is half that of the vapour of solid trichloride of carbon, showing that in the liquid compound the same proportions of carbon vapour and chlorine are condensed into a volume twice as large as in the solid trichloride, 2 vols. of the vapour of the liquid containing 1 vol. imaginary carbon vapour, and 3 vols. chlorine, and being represented by the formula CCl_3.

The following table exhibits the composition of the chlorides of carbon:—

Chlorides of Carbon.

	Molecular Formulæ.	Molecular Volume.	Molecular Weight.
Monochloride, . . .	C_2Cl_2	2 ?	95·0
Dichloride, . . .	C_2Cl_4	2	166·0
Trichloride (solid), .	C_2Cl_6	2	237·0
„ (liquid), .	CCl_3	2	118·5
Tetrachloride, . . .	CCl_4	2	154·0

119. *Oxychloride of carbon, chlorocarbonic acid, or phosgene gas,* is produced by the direct combination of equal volumes of carbonic oxide and chlorine gases under the influence of sunlight (whence its last name), when the mixture condenses to half its volume of a colourless gas, condensable by cold, having a very peculiar pungent smell, and fuming strongly when exposed to moist air, decomposing the moisture and producing hydrochloric acid; $CO.Cl_2 + H_2O = CO_2 + 2HCl$. It is not a true acid, for it is decomposed by bases, producing chlorides and carbonates. It is sometimes found useful in chemical research for removing hydrogen from organic compounds, and introducing carbonic oxide, or its elements, into its place. Its action on ammonia affords an example of this—



$$4(NH_3) + CO.Cl_2 = \underset{\text{Urea.}}{COH_4N_2} + \underset{\text{Hydrochlorate of ammonia.}}{2(NH_3.HCl)}$$

* When vapour of dichloride of carbon is mixed with hydrogen, and passed through a red-hot tube, olefiant gas and hydrochloric acid are produced. The tetrachloride, under similar circumstances, yields marsh-gas.

in which two molecules of NH_3 have been decomposed, two atoms of the hydrogen having been removed in the form of hydrochloric acid, and replaced by a molecule of carbonic oxide.

120. *Chloride of silicon*, unlike the chlorides of carbon, may be formed by the direct union of silicon with chlorine at a high temperature; but it is best prepared by passing dry chlorine over a mixture of artificial silica and charcoal, heated to redness in a porcelain tube connected with a receiver kept cool by a freezing-mixture. Neither carbon nor chlorine separately will act upon the silica, but when they are employed together, the carbon removes the oxygen and the chlorine combines with the silicon—$SiO_2 + C_2 + Cl_4 = SiCl_4 + 2CO$.

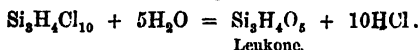
The chloride of silicon is a colourless heavy liquid (sp. gr 1·52) which is volatile (boiling point, 138° F.), and fumes when exposed to air, the moisture of which decomposes it, yielding hydrochloric and silicic acids—



$$SiCl_4 + 2H_2O = SiO_2 + 4HCl.$$

Although it has received no practical application on a large scale, the chloride of silicon is valuable to the chemist as a convenient source of compounds of silicon, which could not easily be procured from the very unchangeable silicic acid.

By passing hydrochloric acid over silicon heated to redness, a very remarkable liquid is obtained, which is much more volatile than the chloride of silicon (boiling point, 108° F.), and, unlike most chlorine compounds, is inflammable, burning with a greenish flame, and producing silica and hydrochloric acid. It fumes strongly in air, and is decomposed by water, yielding hydrochloric acid, and the substance termed leukone. The composition of this liquid appears to be $Si_3H_4Cl_{10}$, and its production would be represented by the equation $Si_3 + 10HCl = Si_3H_4Cl_{10} + H_6$. Its decomposition by water would be explained by the equation—



$$\underset{}{Si_3H_4Cl_{10}} + 5H_2O = \underset{\text{Leukone.}}{Si_3H_4O_5} + 10HCl.$$

The *chloride of boron* (BCl_3) is similar in its general character to the chloride of silicon, and is prepared by a similar process, but it is a gas instead of a liquid at ordinary temperatures.

121. *Chloride of nitrogen* is the name usually given to the very explosive compound before referred to as being produced by the action of chlorine on sal-ammoniac. Its composition is somewhat uncertain; its explosive character rendering its exact analysis very difficult. Some chemists regard it as NCl_3, that is, ammonia in which all the hydrogen has been displaced by chlorine, whilst others believe it to contain hydrogen, regarding it as derived from two molecules of ammonia ($NH_3.NH_3$), by the substitution of five atoms of chlorine for five of hydrogen ($NCl_3.NHCl_2$).

It is a yellow, heavy, oily liquid (sp. gr. 1·65), which volatilises easily, yielding a vapour of very characteristic odour, which affects the eyes. When heated to about 200° F. it explodes with great violence, emitting a loud report and a flash of light. Its instability is, of course, attributable to the feeble attraction which holds its elements together; and the violence of the explosion, to the sudden expansion of a small volume of the liquid into a large volume of nitrogen, chlorine, and perhaps hydrochloric acid. As might be expected, its explosion is at once brought about by contact with substances which have an attraction for chlorine, such as phosphorus and arsenic; the oils and fats cause its explosion, probably by virtue of their hydrogen; oil of turpentine explodes it with greater certainty than the fixed oils. Alkalies also decompose it violently; whilst acids, having

no action upon the chlorine, are not so liable to explode it. At 160° F. this substance has actually been distilled without explosion.

Although practically unimportant, the violent explosive properties of this substance render it so interesting that it may be well to give some directions for its safe preparation.

Preparation of chloride of nitrogen.—Dissolve 4 oz. of sal-ammoniac in 48 oz. (measured) of water, in a porcelain dish, at a gentle heat. Filter the solution, and pour it into a shallow *leaden* dish (A, fig. 187), previously cleaned from all grease by boiling a little solution of potash in it. Place in the solution a smaller leaden dish (B) (capacity, 1½ oz.), cleaned in the same way, and furnished with a copper wire handle.



Fig. 187.

Cut off the neck of a Florence flask (by scratching with a file, and leading the crack round with a red-hot iron), clean it by boiling a little potash in it, rinse it in water, and attach it to a string, so that it may be suspended, in an inverted position, upon a stand.

When the temperature of the solution of sal-ammoniac has fallen to nearly 90° F., fill the Florence flask with water in the pneumatic trough, and displace the water by chlorine, passed up from a gas bottle free from grease. Close the flask with a watch-glass placed under the orifice, and suspend it by the string from a stand (fig. 188), so that its mouth may be about an inch below the surface of the solution of sal-ammoniac, and immediately over the centre of the small leaden dish. Remove the watch-glass, and let the whole arrangement be placed where the explosion can do no harm. The solution will soon begin to absorb the chlorine and to rise in the flask, whilst yellow oily globules form upon its surface, occasionally collecting into a larger one, which falls through the solution into the small leaden dish. When the flask is nearly filled with the solution which will require about twenty minutes, gently raise the flask, from a distance, by hooking the string with a wire at the end of a long stick, and allow the solution to flow gently out of it into the leaden dish. Place the flask at a safe distance, lest there should be any chloride of nitrogen still clinging to it. Examine the leaden dishes to see where the oily globules have fallen, lifting out the smaller dish by hooking its wire handle with a long stick. Explode the globules from a safe distance with a stick dipped in turpentine. A good explosion will throw the solution up several feet, and will raise a large leaden dish several inches into the air, indenting it deeply at the seat of the explosion.

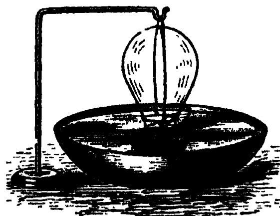


Fig. 188.

Another method of preparing the chloride, when it is not desired to examine it closely, but merely to witness the explosion, consists in acting upon sal-ammoniac with solution of hypochlorous acid; but as this does not succeed in a leaden vessel, and must be performed in glass or porcelain, the action should be conducted at a distance from the operator, lest he be wounded by the fragments of the vessel.

Fifty grains of red oxide of mercury are very finely powdered, and thrown into a pint bottle of chlorine together with ¼ oz. (measured) of water. The stopper is replaced, and the bottle well shaken, loosening the stopper occasionally, as long as the chlorine is absorbed. The solution of hypochlorous acid thus produced is filtered from the residual oxychloride of mercury, and poured into a clean *thumb-glass* (fig. 189). A lump of sal-ammoniac weighing 20 grains is then dropped into the solution, and the glass is placed in a safe situation where the explosion will do no harm. After the lapse of twenty minutes, the chloride of nitrogen may be exploded from a safe distance (9 feet) by touching it with a stick dipped in turpentine. The glass will be shattered into very small fragments, and the operator will be safer behind a screen, unless protected by a fencing-mask and leather gloves.

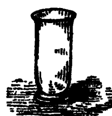
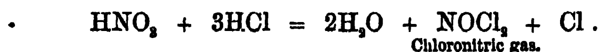


Fig. 189.

122. *Aqua regia.*—This name has been bestowed upon the mixture of

(1 measure of) nitric, and (3 measures of) hydrochloric acid (*nitromuriatic acid*) which is employed for dissolving gold, platinum, and other metals which are not soluble in the separate acids. If a little gold leaf be placed in hydrochloric and nitric acids contained in separate glasses, the metal will remain unaffected even on warming the acids, but if the contents of the glasses be mixed, the gold will be immediately dissolved by the chlorine which is liberated in the action of the acids upon each other—



$$HNO_3 + 3HCl = 2H_2O + \underset{\text{Chloronitric gas.}}{NOCl_2} + Cl.$$

The *chloronitric gas* which is formed does not act upon the gold, but is evolved as a red gas, condensable in a freezing mixture to a dark red liquid. It has a very peculiar odour, and is decomposed by contact with water into hydrochloric acid and nitric peroxide—



$$NOCl_2 + H_2O = 2HCl + NO_2.$$

A similar, though somewhat less volatile substance, called *chloronitrous gas* and having the formula NOCl, is produced by mixing 2 volumes of nitric oxide with 1 volume of chlorine; it condenses to a red liquid at 0° F.; it is also produced in small quantity by the action of hydrochloric acid on nitric acid; $HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2$.

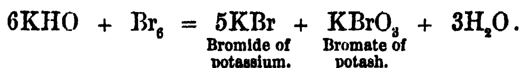
BROMINE.

Br = 80 parts by weight.

123. It generally happens that elements between which any strong family likeness exists are found associated in nature. This remark particularly applies to the three elements—chlorine, bromine, and iodine, all of which are found in sea water, though the first predominates to such an extent that the others for a long time escaped notice. Bromine was brought to light in the year 1826 by Balard in the examination of *bittern*, which is the liquid remaining after the chloride of sodium and some other salts have been made to crystallise by evaporating sea water, which contains only about one grain of bromine per gallon, in the forms of bromide of magnesium and bromide of sodium. It is also extracted from the waters of certain mineral springs, as those of Kreuznach and Kissingen, which contain much larger quantities of bromine, either as bromide of potassium or of sodium or magnesium. During the last few years, much bromine has been obtained from the mother-liquors of the salt-works at Stassfurth, and from saline springs in the United States.

In extracting the bromine from these waters, advantage is taken of the circumstance that chlorine is capable of displacing bromine from its combinations with the metals. After most of the other salts, such as chloride of sodium, sulphate of soda, and sulphate of magnesia, which are less soluble than the bromides, have been separated from the water by evaporation and crystallisation, the remaining liquid is subjected to the action of chlorine gas, when it acquires an orange colour, due to the liberation of the bromine; KBr + Cl = KCl + Br. The bromine thus set free exists now diffused through a large volume of water which cannot be separated from it in the usual way by evaporation, because bromine is itself very volatile. An ingenious expedient is therefore resorted to of shaking the orange liquid briskly with ether, which has a greater solvent

power for bromine than is possessed by water, and therefore abstracts it from the aqueous solution; since ether does not mix to any great extent with water, it now rises to the surface of the liquid, forming a layer of a beautiful orange colour, due to the bromine which it holds in solution. This orange layer is carefully separated, and shaken with solution of potash, which immediately destroys the colour by removing the bromine, leaving the ether to rise to the surface in a pure state, and fit to be employed for abstracting the bromine from a fresh portion of the water. The action of the bromine upon potash is precisely similar to that of chlorine—



$$6KHO + Br_6 = \underset{\text{Bromide of potassium.}}{5KBr} + \underset{\text{Bromate of potash.}}{KBrO_3} + 3H_2O.$$

After the solution of potash has been several times shaken with the ethereal solution of bromine, and has become highly charged with this element, it is evaporated so as to expel the water, leaving a solid residue containing the bromide of potassium and bromate of potash. This saline mass is strongly heated to decompose the bromate of potash, and convert it into bromide of potassium—$KBrO_3 = KBr + O_3$.

From this salt the bromine is extracted by distilling it with binoxide of manganese and sulphuric acid, when the potassium is oxidised at the expense of the binoxide of manganese, and the bromine is liberated and condensed in a receiver kept cool by iced water—



$$2KBr + MnO_2 + 2(H_2O.SO_3) = K_2O.SO_3 + MnO.SO_3 + 2H_2O + Br_2.$$

The aspect of the bromine so produced is totally different from that of any other element, for it distils over in the liquid condition, and preserves that form at ordinary temperatures, being the only liquid non-metallic element. Its dark red-brown colour, and the peculiar orange colour of the vapour which it exhales continually, are also characteristic; but, above all, its extraordinary and disagreeable odour, from which it derives its name (*βρῶμος, a stench*), leaves no doubt of its identity. The odour has some slight resemblance to that of chlorine, but is far more intolerable, often giving rise to great pain, and sometimes even to bleeding at the nose.

Liquid bromine is thrice as heavy as water (sp. gr. 2·96), and boils at 145° F., yielding a vapour 5½ times as heavy as air (sp. gr. 5·54). It may be frozen at −12° F. to a brown crystalline solid. It requires 33 times its weight of cold water to dissolve it, and is capable of forming a crystalline hydrate ($Br.5H_2O$) corresponding to hydrate of chlorine.

In its bleaching power, its aptitude for direct combination, and its other chemical characters, it very closely resembles chlorine—so closely, indeed, that it is difficult to distinguish, in many cases, between the compounds of chlorine and bromine with other substances, unless the elements themselves be isolated. A necessary consequence of so great a similarity is, that very little use has been made of bromine, since the far more abundant chlorine fulfils nearly all the purposes to which bromine might otherwise be applied. In the daguerreotype and photographic arts, however, some special applications of bromine have been discovered, and for some chemical operations, such as the determination of the illuminating hydrocarbons in coal-gas, bromine is sometimes preferred to chlorine. It has also been used in America as a disinfectant. The bromides of potas-

sium and ammonium are frequently employed in medicine. In the composition of their compounds, chlorine and bromine exhibit great analogy.

Hypobromous acid has been obtained in solution by shaking oxide of mercury with water and bromine. The solution is very unstable, decomposing, especially when heated, with liberation of bromine and formation of bromic acid. The action of bromine upon diluted solutions of the alkalies, and upon the alkaline earths, produces bleaching liquids similar to those formed by chlorine.

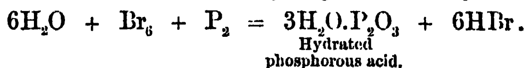
Bromic acid ($HBrO_3$) can be prepared in a similar manner to chloric acid, to which it has a great general resemblance, the bromates being also similar to the chlorates.

124. *Hydrobromic acid* ($HBr = 81$ parts by weight $= 2$ vols.).—The inferiority of bromine to chlorine in chemical energy is well exemplified in its relations to hydrogen, for the vapour of bromine mixed with hydrogen will not explode under the action of flame or of the electric spark, like the mixture of chlorine and hydrogen. Direct combination may, however, be slowly induced by contact with heated platinum.

When it is attempted to prepare this acid by distilling bromide of sodium or potassium with sulphuric acid (as in the preparation of hydrochloric acid, the inferior stability of hydrobromic acid is shown by the decomposition of a part of it, the hydrogen being oxidised by the sulphuric acid, and the bromine set free; $2HBr + H_2O.SO_3 = 2H_2O + SO_2 + Br_2$.

If a strong solution of phosphoric acid be employed instead of the sulphuric, pure hydrobromic acid may be obtained.

But the most instructive method of obtaining hydrobromic acid consists in attacking water with bromine and phosphorus simultaneously, when the phosphorus takes the oxygen of the water, forming phosphorous acid, and the bromine combines with the hydrogen to form hydrobromic acid—



$$6H_2O + Br_6 + P_2 = \underset{\text{Hydrated phosphorous acid.}}{3H_2O.P_2O_3} + 6HBr.$$

Probably bromide of phosphorus (PBr_3) is formed as an intermediate stage.

The experiment may be made in a W-formed tube (fig. 190), one bend of which contains 40 grains of phosphorus in fragments intermingled with glass moistened with water, whilst the other bend contains 240 grains of bromine (about one drachm). This limb of the tube is corked, and the other furnished with a delivery tube, so that the gas may be collected either by downward displacement or over mercury. The bromine is slightly heated, when it distils over to the moist phosphorus, and hydrobromic acid is evolved. A moderate heat should afterwards be applied to the moist glass, to expel part of the hydrobromic acid from the water.

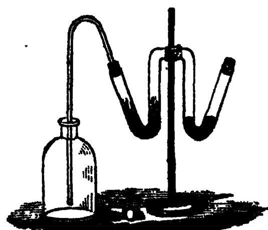


Fig. 190.—Preparation of hydrobromic acid.

Hydrobromic acid is very similar to hydrochloric acid; it liquefies at $-92°$ F., and has been solidified by a still lower temperature, which is not the case with hydrochloric acid. Like that gas it is very soluble in water, and the solution acts upon metals and their oxides in the same manner as hydrochloric acid. Chlorine removes the hydrogen from hydrobromic acid, liberating bromine, which it converts into *chloride of bromine* if employed in excess.

Bromide of nitrogen has been obtained by the action of bromide of

potassium upon chloride of nitrogen, which it resembles in general character and explosive properties.

Chloride of bromine is a very volatile yellow liquid of pungent odour. Its composition is not certainly known. That chlorine should unite directly with bromine, which it so much resembles in chemical character, illustrates its great tendency to direct chemical combination.

IODINE.

I = 127 parts by weight.

125. Iodine is contained in sea water in even smaller quantity than bromine, but the iodide of sodium appears to constitute a portion of the necessary food of certain varieties of sea-weed, which extract it from the sea-water, and concentrate it in their tissues. The ash remaining after sea-weed has been burnt was long used, under the name of *kelp*, in soap-making, because it contains a considerable quantity of carbonate of soda; and in the year 1811, Courtois, a soap-boiler of Paris, being engaged in the manufacture of soda from kelp, obtained from the waste liquors a substance which possessed properties different from those of any form of matter with which he was acquainted. He transferred it to a French chemist, Clement, who satisfied himself that it was really a new substance, and Gay-Lussac and Davy having examined it still more closely, it took its rank among the non-metallic elementary substances, under the name of iodine (ἰώδης, *violet-coloured*), conferred upon it in allusion to the magnificent violet colour of its vapour.

This history of the discovery of iodine affords a very instructive example of the advantage of training persons engaged in manufactures to habits of accurate observation, and, if possible, of accurate chemical observation; for had Courtois passed over this new substance as accidental, or of no consequence, the community would have lost, at least for some time, the benefits derived from the discovery of iodine.

For some years the new element was only known as a chemical curiosity, but an unexpected demand for it at length arose on the part of the physician, for it had been found that the efficacy of the ashes of sponge, which had long been used in some particular maladies, was due to the small quantity of iodine which they contained, and it was, of course, thought desirable to place this remedy in the hands of the medical profession in a purer form than the ash of sponge, where it is associated with very large quantities of various saline substances. Much more recently the demand for this element has greatly increased, on account of its employment in photography, and large quantities of it are annually produced from kelp, the collection and burning of which affords occupation to the very poor inhabitants of some parts of the coasts of Ireland and Scotland, who would otherwise have been thrown out of work when soda began to be manufactured from common salt, and the demand for kelp as the source of that alkali had ceased. The sea-weed is spread out to dry, and burnt in shallow pits at as low a temperature as possible, for the iodide of sodium is converted into vapour and lost if the temperature be very high.* The ash, which is left in a half-fused state, is broken into fragments and treated with hot water, which dissolves about half of it, leaving a residue, consisting of carbonate and sulphate of lime, sand, &c. The whole of the

* The sea-weed is often only charred and not incinerated, so as to avoid loss of iodine.

iodide of sodium is contained in the portion dissolved by the water, but is mixed with much larger quantities of sulphate of soda, carbonate of soda, chloride of potassium, hyposulphite of soda, and sulphide of sodium. A portion of the water is expelled by evaporation, when the sulphate of soda, carbonate of soda, and chloride of potassium, being far less soluble than the iodide of sodium, crystallise out. In order to decompose the hyposulphite of soda and the sulphide of sodium, the liquid is mixed with an eighth of its bulk of oil of vitriol, which decomposes these salts, evolving sulphurous and hydrosulphuric acid, with deposition of sulphur, and forming sulphate of soda, which is deposited in crystals. The liquor thus prepared is next mixed with binoxide of manganese, and heated in a leaden retort (fig. 191), placed in a sand-bath, when the iodine is evolved as a magnificent purple vapour, which condenses in the globular glass receivers in the form of dark grey scales with metallic lustre, and having considerable resemblance to black lead. The liberation of the iodine is explained by the following equation—

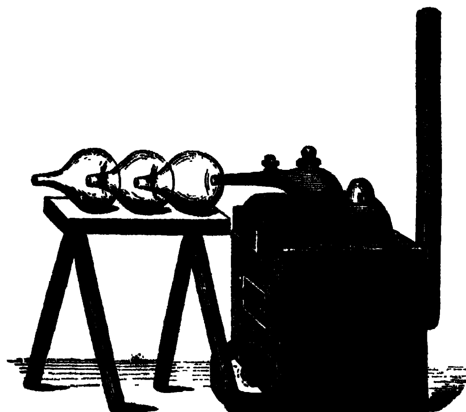


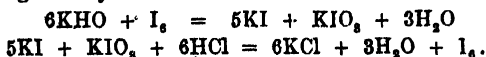
Fig. 191.—Extraction of iodine.



$$2NaI + MnO_2 + 2(H_2O.SO_3) = Na_2O.SO_3 + MnO.SO_3 + 2H_2O + I_2.$$

The distillation is conducted at a temperature below 212°, to avoid the liberation of chlorine from the chloride of sodium, and the consequent formation of chloride of iodine.

Several processes have been devised to render the extraction of the iodine from the concentrated solution of kelp easier and more economical. The most promising is very similar to that employed for separating bromine (p. 172). The iodine is liberated by chlorine, and extracted from the liquid by shaking it with benzole; by treating the benzole with solution of potash, the iodine is converted into a mixture of iodide of potassium and iodate of potash, from which the iodine may be precipitated by acidifying with hydrochloric acid.



$$6KHO + I_6 = 5KI + KIO_3 + 3H_2O$$
$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + I_6.$$

The features of this element are extremely well marked; its metallic lustre and peculiar odour sufficiently distinguish it from all others, and the effect of heat upon it is very striking, in first easily fusing it (at 225° F.), and afterwards converting it (boiling point, 347° F.) into the most exquisitely purple vapour, which is nearly nine times as heavy as air (sp. gr. 8·72), and condenses upon a cool surface in shining scales. It stains the skin intensely brown if handled. The specific gravity of solid iodine is 4·95.

When iodine is shaken with cold water a very small quantity is dissolved, forming a light brown solution, which decomposes slowly at the ordinary temperature, the iodine combining with the hydrogen of the

water. Hot water dissolves a larger quantity, but alcohol is one of the best solvents for iodine, producing a dark red-brown solution (*tincture of iodine*) from which part of the iodine may be precipitated by adding water. A solution of iodide of potassium also dissolves iodine freely. Benzole and bisulphide of carbon dissolve it abundantly, producing fine violet-red solutions, which deposit the iodine, if allowed to evaporate spontaneously, in minute rhombic octahedral crystals aggregated into very beautiful fern-like forms. If an extremely weak aqueous solution of iodine be shaken with a little bisulphide of carbon, the latter will remove the iodine from the solution, and on standing, will fall to the bottom of the liquid, having a beautiful violet colour. By dissolving a large quantity of iodine in bisulphide of carbon, a solution is obtained which is perfectly opaque to rays of light, though it allows heat-rays to pass freely, and is, therefore, of great value in physical experiments. A solution of iodine in bichloride of carbon is also used for the same purpose.

Existing, as iodine does, in very minute quantity in the water from various natural sources, it would often be overlooked if the chemical analyst did not happen to possess a test of the most delicate description for it.

Iodine, in the uncombined state, dyes starch of a beautiful blue colour, as may be proved by heating a grain or two of the element with water, and adding to the solution a little thin starch (see p. 53), or by placing a minute fragment of iodine in a stoppered bottle, and suspending in it a piece of paper dipped in thin starch. This test, however, though sensitive to the smallest quantity of free iodine, gives no indication whatever with iodine in combination, as it always exists in nature; in order, therefore, to test for iodine, a little starch-paste is added to the suspected liquid, and then a drop of a weak solution of chlorine, which will set free the iodine, and cause the production of the blue colour. Characters written on paper with a brush dipped in a mixture of iodide of potassium and starch, are brought out in blue by pouring a little chlorine-gas upon them. It is necessary, however, carefully to avoid adding too much chlorine, since it would immediately destroy the colour of the iodised starch. Alkalies also bleach it, and the colour of a mixture of the iodised starch with water is removed by heating, but returns in great measure when the solution cools.

Though very closely connected with chlorine and bromine in its general chemical relations, there are several points in the history of iodine which cause it to stand out in marked contrast by the side of these elements. The attraction which binds it to hydrogen and the metals is certainly weaker than that exerted by chlorine and bromine, so that either of these is capable of displacing it from its compounds, and its bleaching properties are very feeble. On the other hand, it exhibits a more powerful tendency to unite with oxygen, for boiling nitric acid converts it into iodic acid (I_2O_5), though this oxidising agent would not affect chlorine or bromine.

Some of the compounds of iodine with the metals are remarkable for their beautiful colours. The *iodide of mercury*, produced by mixing solutions of iodide of potassium and chloride of mercury, forms a fine scarlet precipitate, which dissolves in an excess of iodide of potassium to a *colourless* solution.

If this iodide of mercury be collected on a filter, washed and dried, it will be found, on heating a portion of it in a test-tube, that it acquires a fine yellow colour and sublimes in golden yellow crystals, which resume the original red colour when rubbed with a glass rod. If it be spread upon paper and gently heated, the scarlet iodide becomes yellow, but the red colour returns on rubbing it with the thumb-

nail. These changes of colour are attended by an alteration in crystalline form, but not in the chemical composition of the iodide of mercury. This iodide is used in painting under the name of *pure scarlet* or *iodine scarlet*, but the colour is not durable.

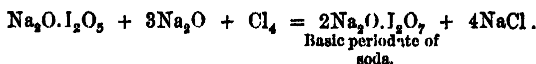
Iodide of lead has a bright yellow colour, as may be seen by precipitating iodide of potassium with a solution of acetate of lead. The precipitate is dissolved by boiling with water (especially on adding a little hydrochloric acid), forming a colourless solution, from which the iodide of lead crystallises in very brilliant golden scales on cooling. *Iodide of silver* is produced as a yellow precipitate when nitrate of silver is added to iodide of potassium. The bromide and chloride of silver would form white precipitates.

126. *Oxides of iodine.*—Although the compound I_2O, corresponding to hypochlorous acid, is believed to exist, it has never yet been obtained in a separate state, the only known oxides of iodine being iodic acid (I_2O_5) and periodic acid (I_2O_7?) which has only been obtained in the hydrated state.

Iodic acid.—It is most easily prepared by boiling iodine with the strongest nitric acid in a long-necked flask, when it is dissolved in the form of iodic acid which is left on evaporating the nitric acid, as a white mass. This may be purified by dissolving in water and crystallising, when the iodic acid forms white hexagonal tables, which have the composition $H_2O.I_2O_5.2Aq$. Heated to 266° F., they become $H_2O.I_2O_5$, and at 360° F. the whole of the water is expelled, leaving anhydrous iodic acid, which is decomposed at about 700° F. into iodine and oxygen. The anhydrous iodic acid oxidises combustible bodies, but not with any great violence. The hydrate is far more stable than the hydrated chloric and bromic acids. Its solution first reddens litmus paper, and afterwards bleaches it by oxidation. Its salts, the *iodates*, are less easily soluble in water than the chlorates and bromates, which they resemble in their oxidising action upon combustible bodies. They are all decomposed by heat, evolving oxygen, and sometimes even iodine, showing how much inferior this element is to chlorine and bromine in its attraction for metals.

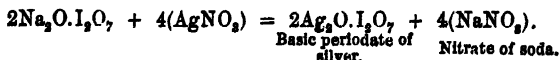
It is a remarkable feature of the iodates, that some of them contain two or even three molecules of iodic acid to one of base. Thus there are three iodates of potash, $K_2O.I_2O_5$ (or KIO_3) $K_2O.2I_2O_5$, and $K_2O.3I_2O_5$. No such compounds are known in the cases of chloric and bromic acids.

Periodic acid is obtained from the basic periodate of soda formed by passing chlorine through a mixture of iodate of soda and free soda, when the latter is decomposed, its sodium being abstracted by the chlorine, whilst its oxygen converts the iodic acid into periodic acid—



$$Na_2O.I_2O_5 + 3Na_2O + Cl_4 = \underset{\text{Basic periodate of soda.}}{2Na_2O.I_2O_7} + 4NaCl.$$

This periodate of soda is deposited, being sparingly soluble in water, a most unusual circumstance with salts of soda. By dissolving it in nitric acid, and adding nitrate of silver, a basic periodate of silver is obtained, which is yellow when precipitated from cold, and red from hot solutions—



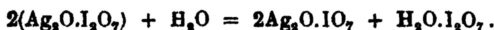
$$2Na_2O.I_2O_7 + 4(AgNO_3) = \underset{\text{Basic periodate of silver.}}{2Ag_2O.I_2O_7} + \underset{\text{Nitrate of soda.}}{4(NaNO_3)}.$$

When the silver salt is dissolved in nitric acid, it is decomposed into nitrate of silver, which remains in solution, and neutral periodate of silver, which is deposited in crystals—



$$2Ag_2O.I_2O_7 + H_2O.N_2O_5 = Ag_2O.I_2O_7 + Ag_2O.N_2O_5 + H_2O.$$

When neutral periodate of silver is boiled with water, it again yields the insoluble basic periodate of silver, and hydrated periodic acid is found in the solution—

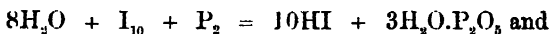


$$2(Ag_2O.I_2O_7) + H_2O = 2Ag_2O.IO_7 + H_2O.I_2O_7.$$

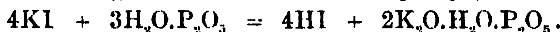
On evaporating the solution, the hydrated periodic acid is deposited in prismatic crystals having the composition $H_2O.I_2O_7.4Aq$, which lose their water at about 320° F., and are decomposed into iodic acid and oxygen at 400° F. The solution of periodic acid, of course, exhibits oxidising properties.

The *periodates* are remarkable for their sparing solubility in water; they are easily decomposed by heat, like the iodates. It will have been remarked, in the above account of the preparation of periodic acid, that this acid exhibits a great tendency to the formation of basic salts, whilst iodic acid is remarkable for its acid salts.

127. *Hydriodic acid* (HI = 128 parts by weight = 2 vols.).—Iodine vapour combines with hydrogen, under the influence of heated platinum, to form hydriodic acid gas. The gas is best prepared by decomposing water with iodine in the presence of phosphorus, so as to produce hydriodic acid and phosphoric acid, which is allowed to act upon iodide of potassium in order to produce more hydriodic acid—



$$8H_2O + I_{10} + P_2 = 10HI + 3H_2O.P_2O_5 \text{ and}$$



$$4KI + 3H_2O.P_2O_5 = 4HI + \underset{\text{Phosphate of potash.}}{2K_2O.H_2O.P_2O_5}.$$

100 grains of iodide of potassium are dissolved in 50 grains of water in a retort (fig. 192), and 200 grains of iodine are added; when this has dissolved, 10 grains of phosphorus are introduced, and the mixture heated very gradually, the gas being collected by downward displacement in stoppered bottles, which must be placed in readiness, as the gas comes off very rapidly. These quantities will fill four pint bottles with the gas.

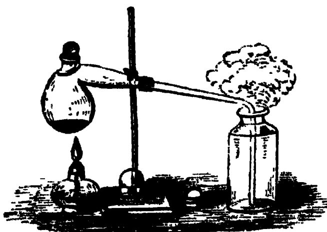
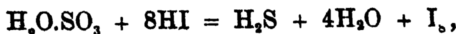


Fig. 192.—Preparation of hydriodic acid.

Hydriodic acid gas is very similar in its properties to hydrochloric and hydrobromic acids, fuming strongly in moist air, very readily absorbed by water, liquefied only under strong pressure, and solidified by extreme cold. It is much heavier, its specific gravity being 4·44. If a bottle of hydriodic acid gas be placed in contact with a bottle containing chlorine or bromine vapour diluted with air (fig. 149), it will be instantly decomposed, with separation of the beautiful violet vapour of iodine.

The aqueous solution of hydriodic acid is most conveniently prepared by passing hydrosulphuric acid gas through water in which iodine is suspended, $H_2S + I_2 = 2HI + S$, the separated sulphur being filtered off, and the solution boiled to expel the excess of hydrosulphuric acid. Solution of hydriodic acid differs greatly from hydrochloric and hydrobromic acids, in being decomposed by exposure to air, its hydrogen being oxidised and iodine separated, which dissolves in the liquid and renders it brown.

This tendency of the hydrogen of hydriodic acid to combine with oxygen renders that acid a powerful *reducing* agent. It is even capable of converting hydrated sulphuric acid into hydrosulphuric acid—



$$H_2O.SO_3 + 8HI = H_2S + 4H_2O + I_8,$$

so that when iodide of potassium is heated with concentrated sulphuric acid, hydrosulphuric acid is evolved in considerable quantity.

The action of hydriodic acid upon the metals and their oxides is generally similar to that of the other hydrogen acids.

When potassium is heated in a measured volume of hydriodic acid, the iodine is removed, and the hydrogen occupies half the original volume. Hence 1 volume of hydrogen is combined with 1 volume of iodine vapour in 2 volumes of hydriodic acid.

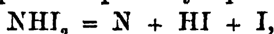
Like chlorine and bromine, iodine is capable of displacing hydrogen from many organic compounds, and of taking its place, but its action in this respect is much feebler. The circumstance that the organic compounds containing iodine are generally much less volatile, and therefore more manageable than those of chlorine and bromine, leads to the extensive employment of this element in researches upon organic substances.

With olefiant gas, iodine forms a crystalline solid compound ($C_2H_4I_2$) corresponding to Dutch liquid (p. 92), and from this compound a yellow unstable aromatic liquid has been obtained, which is believed to be an *iodide of carbon.*

128. *Iodide of nitrogen.*—The action of chlorine, bromine, and iodine upon ammonia, exemplifies the difference in their attraction for hydrogen; for whilst chlorine and bromine, acting upon ammonia, cause the liberation of a certain amount of nitrogen, iodine simply removes two-thirds of the hydrogen, and itself fills up the vacancies thus occasioned, no nitrogen being liberated, $NH_3 + I_4 = NHI_2 + 2HI$; the hydriodic acid thus formed combining with more ammonia to form hydriodate of ammonia.

To prepare the iodide of nitrogen, 20 grains of iodine are rubbed to powder in a mortar and mixed with half an ounce (measured) of strong ammonia; the mortar is covered with a glass plate, and after about half an hour the iodide of nitrogen is collected in separate portions upon four filters, which are allowed to drain and spread out to dry. The brown solution contains iodine dissolved in hydriodate of ammonia.

The iodide is a black powder, which explodes with a loud report even when touched with a feather, emitting fumes of hydriodic acid and purple vapour of iodine; its explosion is probably represented by the equation—



$$NHI_2 = N + HI + I,$$

its violence being accounted for by the sudden evolution of a large volume of gas and vapour from a small volume of solid. Even when allowed to fall from the height of a few feet upon the surface of water, it explodes if perfectly dry. In the moist state it slowly undergoes decomposition.

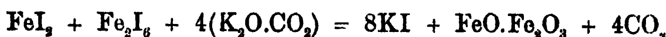
129. Iodine forms two compounds with chlorine, the *protochloride of iodine* (ICl) and the *terchloride* (ICl_3). The former is a brown volatile liquid of irritating odour, obtained by distilling 1 part of iodine with 4 parts of chlorate of potash.

The terchloride forms fine red needle-like crystals, and is produced when iodine is acted upon with an excess of chlorine. *Bromides of iodine* have also been obtained, but their composition is not well known.

130. *Iodide of potassium* (KI = 166 parts by weight). This salt is the most useful compound of iodine, being largely employed in medicine and in photography. It is generally prepared by decomposing iodide of iron with carbonate of potash.

The *iodide of iron* (also a useful medicine) is made by placing two parts of iodine in contact with one part of iron filings and ten parts of water. The iodine combines with part of the iron, evolving considerable heat, and producing the iodide of iron (FeI_2).

The liquid is decanted from the excess of iron, and one-third of the weight of iodine previously employed is dissolved in it. In this way, two-thirds of the iodide of iron are converted into per-iodide (Fe_2I_6), so that the solution contains a mixture of one molecule of the iodide (FeI_2) and one of the per-iodide (Fe_2I_6). It is now boiled, and carbonate of potash is gradually added as long as it causes a dark green precipitate of magnetic oxide of iron—



$$FeI_2 + Fe_2I_6 + 4(K_2O.CO_2) = 8KI + FeO.Fe_2O_3 + 4CO_2$$

the carbonic acid is evolved with effervescence, and if the solution be filtered and evaporated, it deposits beautiful cubical (or sometimes octahedral) crystals, which are generally milk-white and opaque, but occasionally quite transparent. Pure iodide of potassium remains dry in ordinary air, but if an excess of carbonate of potash is employed in its preparation, the crystals retain some of that salt and become damp when exposed to air. The iodide of potassium dissolves easily in water and alcohol. If the solution be pure, it does not become coloured when mixed with pure hydrochloric acid; but if any iodate of potash be present in it, a brownish colour will be produced, due to iodine liberated in the action of the iodic acid upon the hydriodic acid; $I_2O_5 + 10HI = I_{12} + 5H_2O$. The iodate of potash is liable to be present in those specimens which are prepared by dissolving iodine in potash, to obtain a mixture of iodide of potassium and iodate of potash (see p. 176), the latter salt being afterwards decomposed by heat.

FLUORINE.

F = 19 parts by weight.

131. The most ornamental mineral substance occurring in any abundance in this country is known as *fluor spar* or *Derbyshire spar* (fluoride of calcium), and is found with several beautiful shades of colour—blue, purple, violet, or green, and sometimes perfectly colourless, either in large masses, or in crystals, which have the form of a cube or of some solid derived from it. The use of this mineral as a flux in smelting ores dates from a very remote period, and from this use the name fluor appears to have been originally derived, but we have no record of its chemical examination till about a century since, when Margraf found his glass retort powerfully corroded in distilling this mineral with sulphuric acid, and Scheele soon after announced that it contained lime and *fluoric acid;* but though this chemist had fallen into the error to which analysts are continually liable, of mistaking products for educts, his experiments, as they were afterwards perfected by Gay-Lussac and Thénard, deserve particular consideration.

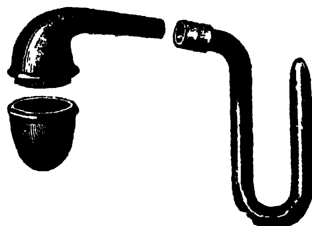
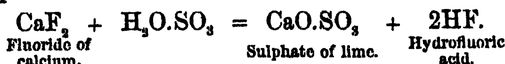


Fig. 193.

132. *Hydrofluoric acid*—(HF = 20 parts by weight).—If powdered fluor spar be mixed with twice its weight of oil of vitriol, and heated in a leaden retort (fig. 193), the neck of which fits tightly into a leaden condensing-tube, cooled in a mixture of ice and salt, a

colourless liquid distils over, and the residue in the retort is found to consist of sulphate of lime—*



$$\underset{\text{Fluoride of calcium.}}{CaF_2} + H_2O.SO_3 = \underset{\text{Sulphate of lime.}}{CaO.SO_3} + \underset{\text{Hydrofluoric acid.}}{2HF.}$$

The colourless liquid (hydrofluoric acid) possesses most remarkable properties; it is powerfully acid, fumes strongly in the air, and has a most pungent irritating odour. If the air is at all warm the liquid begins to boil when taken out of the freezing mixture, and is soon entirely dissipated in vapour (boiling point, 60° F.) Should the operator have the misfortune to allow a drop to fall upon his hand, it will produce a very painful sore, even its vapour producing pain under the finger nails. Its attraction for water is so great, that the acid hisses like red-hot iron when brought in contact with it. But its most surprising property is that of rapidly corroding glass, which has already been alluded to as noticed by Margraf. Experiment soon proved that great analogy existed between the properties of this new acid and those of hydrochloric acid; and Ampère was led to institute a comparison between them, which caused him to adopt the opinion that the acid was a hydrogen acid, containing a new salt radical which he named fluorine; the name of the acid was then changed from fluoric to hydrofluoric acid.

This liquid has since been proved to be a solution of hydrofluoric acid in water, for if it be distilled with anhydrous phosphoric acid, which retains the water, it evolves hydrofluoric acid gas, which resembles hydrochloric acid gas in fuming strongly on contact with moist air, and being eagerly absorbed by water, but has a far more pungent odour. The perfectly dry gas has very little action upon glass.

Pure hydrofluoric acid is prepared by heating dry *hydrofluate of potassium* (KF.HF) to redness in a platinum apparatus. It is then obtained as a colourless liquid which boils at 67° F. and has the specific gravity 0·988 at 55° F. The pure acid scarcely affects metals, excepting potassium and sodium. It corrodes glass, however, rapidly, though its vapour has little action on glass unless moisture is present. It combines eagerly with anhydrous sulphuric and phosphoric acids, with great evolution of heat, a circumstance in which it resembles water, and differs altogether from its more obvious analogue, hydrochloric acid. It is also found that it combines energetically with the fluorides of potassium and sodium, precisely as water combines with the oxides of those metals, whilst nothing of the kind is noticed in the case of hydrochloric acid.

It is remarkable that the solution of hydrofluoric acid, in its concentrated form, is not so heavy as a somewhat weaker acid. Thus, the acid of sp. gr. 1·06 acquires the sp. gr. 1·15 on addition of a little water, but on adding more water its sp. gr. is again reduced. It would hence appear that the acid of 1·15 is a definite hydrate of hydrofluoric acid; its composition corresponds to $HF.2H_2O$. It distils unchanged at 248° F. The solution is generally kept in bottles made of gutta-percha.

The action of hydrofluoric acid upon metals and their oxides resembles that of hydrochloric acid. It dissolves all ordinary metals except gold, platinum, silver, mercury, and lead. Strange to say, it has but little action on magnesium.

* The mineral kryolite (fluoride of aluminum and sodium) may be advantageously substituted for fluor spar, being more easily obtained in a pure state. For preparing the acid on a large scale, iron retorts are employed.

The property which renders this acid so useful to the chemist is its power of dissolving silica even in its most refractory form. When sand or flint reduced to powder is digested in a leaden or platinum vessel with hydrofluoric acid, it is gradually dissolved, and if the solution be evaporated, the whole of the silica will be found to have disappeared in the form of gaseous fluoride of silicon; $SiO_2 + 4HF = SiF_4 + 2H_2O$. If the silicic acid be combined with a base, the metal will be left as a fluoride, decomposable by sulphuric or hydrochloric acid. This renders hydrofluoric acid a most valuable agent in the analysis of the numerous mineral silicates which resist the action of other acids.

The corrosion of glass by hydrofluoric acid is now easily explained. Ordinary glass consists of silicate of soda or potash combined with silicate of lime or oxide of lead. The hydrofluoric acid attacks and removes the silica, and thus eats its way into the glass.

In order to demonstrate the action of this acid upon glass, a glass plate is warmed sufficiently to melt wax, a piece of which is then rubbed over it, until the glass is covered with a thin and pretty uniform coating. Upon this a word or drawing may be engraved with a sharp point so that the lines shall expose the glass. A mixture of powdered fluor spar with concentrated sulphuric acid is then poured over it, and allowed to remain for a quarter of an hour; the acid mixture is washed off, and the plate gently warmed to melt the wax, which may be wiped off with a little tow, when it will be found that the hydrofluoric acid evolved from the mixture has corroded those portions of the glass from which the graver had removed the wax. It has been attempted to apply this process to the production of engravings, but the brittleness of the plate has formed a very serious obstacle.

If a leaden or platinum dish be at hand, it is better to place the glass to be etched over the dish containing the mixture of fluor spar and sulphuric acid exposed to a very gentle heat.

The solution of hydrofluoric acid etches glass without deadening the surface as is the case with the vapour, but a solution of fluoride of potassium or ammonium mixed with sulphuric acid does produce a dead surface and is much used for engraving on glass.

Many ingenious experiments have been made in order to obtain fluorine in the separate state, but it was found that it invariably combined with some portion of the material of the vessel in which the operation was conducted. The most successful of the early attempts to isolate fluorine appears to have been made, at the suggestion of Davy, in a vessel of fluor spar itself, which could not, of course, be supposed to be in any way affected by it. A greenish gas was obtained, possessing chemical properties similar to those of chlorine, but of much higher intensity. The difficulty, however, of obtaining vessels of fluor spar adapted to these experiments appears to have prevented any complete investigation of this most interesting element.

The most recent experiments, in which fluoride of silver was decomposed by iodine, furnished a fluoride of iodine (IF_5) and iodide of silver.

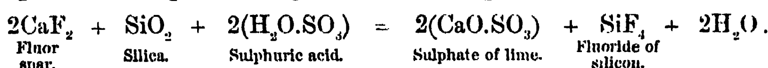
Solutions of the fluorides of potassium and the other alkali metals corrode glass slowly like hydrofluoric acid. These fluorides are capable of combining with the acid; thus fluoride of potassium forms $KF.HF$, which, when dry, is a convenient source of hydrofluoric acid gas when moderately heated. The only fluoride possessed of much practical interest beside the fluoride of calcium is the mineral *kryolite* (*κρυος, frost*), which is a double fluoride of aluminum and sodium ($3NaF.AlF_3$) found abundantly in Greenland, and valuable as a source of aluminum and soda. The *topaz*

contains fluorine, but in what form of combination is not well known; its other constituents are alumina and silica.

Fluorides are also found, though in very small quantity, in sea water, and they have been discovered in plants and animals. Human bone contains about 2 per cent. of fluoride of calcium.

It will be remembered that fluorine is the only element which is not known to form any compound with oxygen.

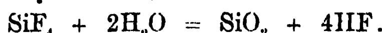
133. *Fluoride of silicon* (SiF_4 = 104 parts by weight = 2 vols.).—If a mixture of powdered fluor spar and glass be heated, in a test-tube or small flask, with concentrated sulphuric acid, a gas is evolved which has a very pungent odour, and produces thick white fumes in contact with the air; it might at first be mistaken for hydrofluoric acid, but if a glass rod or tube be moistened with water and exposed to the gas, the wet surface becomes coated with a white film, which proves, on examination, to be silicic acid. This result originated the belief that the gas consisted of fluoric (now hydrofluoric) acid and silica, but Davy corrected this view by showing that it really contained no oxygen, and consisted solely of silicon and fluorine. The gas is now called the fluoride of silicon, and represents silicic acid in which the oxygen has been displaced by the fluorine; the change of places between these two elements in the above experiment is represented by the subjoined equation—



$$2CaF_2 + SiO_2 + 2(H_2O.SO_3) = 2(CaO.SO_3) + SiF_4 + 2H_2O.$$

Fluor spar. Silica. Sulphuric acid. Sulphate of lime. Fluoride of silicon.

The formation of the crust of silica upon the wetted surface of the glass is due to a decomposition which takes place between the fluoride of silicon and the water, in which the oxygen and fluorine again change places—



$$SiF_4 + 2H_2O = SiO_2 + 4HF.$$

Since this latter equation shows that hydrofluoric acid is again formed, it would be expected that the glass beneath the deposit of silica would be found corroded by the acid; this, however, is not the case, and when the experiment is repeated upon a somewhat larger scale, so that the water which has acted upon the gas may be examined, it will be found to hold in solution, not hydrofluoric acid, but an acid which does not act upon glass, and is composed of hydrofluoric acid and fluoride of silicon, so that the hydrofluoric acid produced when water acts upon the fluoride, combines with a portion of the latter to produce the new acid $2HF.SiF_4$, *hydrofluo-silicic acid.*

For the preparation of fluoride of silicon, 1 oz. of fluor spar and 1 oz. of powdered glass are mixed together, and heated, in a Florence flask, with 7 oz. (measured) of oil of vitriol, the gas being collected in dry bottles by downward displacement (see fig. 177, p. 153. If a little of the gas be poured from one of the bottles into a flask filled up to the neck with water, the surface of the latter will become covered with a layer of silica, so that if the flask be quickly inverted, the water will not pour from it, and will seem to have been frozen. In a similar manner, a small tube filled with water and lowered into a bottle of the gas, will appear to have been frozen when withdrawn. A stalactite of silica some inches in length may be obtained by allowing water to drip gently from a pointed tube into a bottle of the gas. Characters written on glass with a wet brush are rendered opaque by pouring some fluoride of silicon upon them.

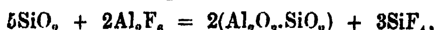
Fluoride of silicon is a substance of some importance in mineralogical chemistry, since, by its aid, certain crystallised minerals may be artificially obtained under conditions which are not unlikely to have attended the production of the natural crystals. Thus, the mineral *staurotide* or *staurolite* (σταυρὸς, *a cross*), or *granatite* or *cross-stone*,

a naturally crystallised compound of alumina and silicic acid, may be obtained by the action of fluoride of silicon upon alternate layers of alumina and silica, heated to whiteness in a porcelain tube. The fluoride of silicon, acting upon the heated alumina, gives silicate of alumina and fluoride of aluminum—



$$3Al_2O_3 + 3SiF_4 = Al_2O_3.3SiO_2 + 2Al_2F_6,$$

the newly-formed fluoride of aluminum, passing over a heated layer of silica, produces more silicate of alumina, regenerating fluoride of silicon—



$$5SiO_2 + 2Al_2F_6 = 2(Al_2O_3.SiO_2) + 3SiF_4,$$

so that a given quantity of the fluoride of silicon will convert an indefinite quantity of silica and alumina into the crystallised staurolite. It appears probable that other crystallised minerals have been formed in a similar manner, by the action of minute quantities of such agents of transformation. The frequent occurrence of minute quantities of fluorides in various minerals may thus have great significance.

134. *Hydrofluo-silicic acid* or *silico-fluoric acid* ($2HF.SiF_4 = 144$ parts by weight).—This acid is only known in the form of a solution, which is obtained by passing fluoride of silicon into water—



$$3SiF_4 + 2H_2O = 2(2HF.SiF_4) \text{ (Hydrofluo-silicic acid) } + SiO_2.$$

The gas must not be passed directly into the water, lest the separated silica should stop the orifice of the tube, to prevent which, the latter should dip into a little mercury at the bottom of the water, when each bubble, as it rises through the mercury into the water, will become surrounded with an envelope of gelatinous silica, and if the bubbles be very regular, they may even form tubes of silica extending through the whole height of the water.

For preparing hydrofluo-silicic acid it will be found convenient to employ a gallon stoneware bottle (fig. 194), furnished with a wide tube dipping into a cup of mercury placed at the bottom of the water. 1 lb. of finely powdered fluor spar, 1 lb. of fine sand, and 64 measured ounces of oil of vitriol, are introduced into the bottle, which is gently heated upon a sand-bath, the gas being passed into about 5 pints of water. After 6 or 7 hours the water will have become pasty, from the separation of gelatinous silica. It is poured upon a filter, and when the liquid has drained through as far as possible, the filter is wrung in a cloth to extract the remainder of the acid solution, which will have a sp. gr. of about 1·078.

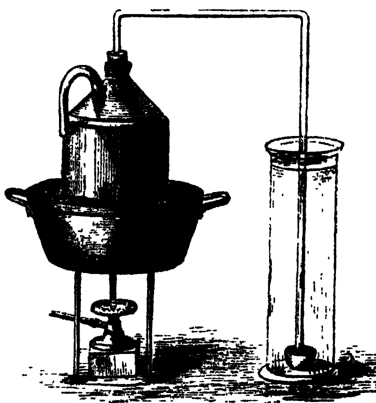


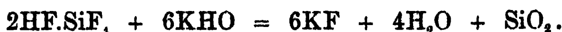
Fig. 194.—Preparation of hydrofluo-silicic acid.

A dilute solution of hydrofluo-silicic acid may be concentrated by evaporation up to a certain point, when it begins to decompose, evolving fumes of fluoride of silicon, hydrofluoric acid remaining in solution and volatilising in its turn if the heat be continued. Of course the solution corrodes glass and porcelain when evaporated in them. If the solution of hydrofluo-silicic acid be neutralised with potash, and stirred, a very characteristic crystalline precipitate of silico-fluoride of potassium is formed—



$$2HF.SiF_4 + 2KHO = 2KF.SiF_4 \text{ (Silico-fluoride of potassium) } + 2H_2O.$$

But if an excess of potash be employed, a precipitate of gelatinous silica will be separated, fluoride of potassium remaining in the solution—



$$2HF.SiF_4 + 6KHO = 6KF + 4H_2O + SiO_2.$$

One of the chief uses of hydrofluo-silicic acid is to separate the potash from its combination with certain acids, in order to obtain these in the separate state.

135. *Fluoride of boron* (BF_3) may be prepared by a process similar to that employed for fluoride of silicon, but it is also obtained by strongly heating a mixture of powdered anhydrous boracic acid with twice its weight of fluor spar in an iron tube—



$$3CaF_2 + B_2O_3 = 3CaO + 2BF_3.$$

The fluoride of boron is a gas which fumes strongly in moist air like the fluoride of silicon. It is absorbed eagerly by water, with evolution of heat. One volume of water is capable of dissolving 700 volumes of fluoride of boron, producing a corrosive heavy liquid (sp. gr. 1·77) which fumes in air, and chars organic substances on account of its attraction for water. This solution is known as *fluoboric* or *borofluoric acid*, and its formation is explained by the equation—



$$2BF_3 + 3H_2O = B_2O_3.6HF \text{ (Fluoboric acid)}.$$

When the solution is heated, it evolves fluoride of boron until its specific gravity is reduced to 1·58, when it distils unchanged.

Hydrofluoboric acid is obtained in solution by adding a large quantity of water to fluoboric acid—



$$4(B_2O_3.6HF) = B_2O_3 + 9H_2O + 6(HF.BF_3) \text{ (Hydrofluoboric acid)}.$$

This acid resembles the hydrofluo-silicic; its hydrogen may be exchanged for metals to form *borofluorides*.

136. *General review of chlorine, bromine, iodine, and fluorine.*—These four elements compose a natural group, the members of which are connected, by the similarity of their chemical properties, far more closely than those of any other group of elements. They are usually styled the *halogens*, from their tendency to produce salts resembling sea-salt in their composition (*ἅλς, the sea*), and such salts are called *haloid salts*. These elements are also called *salt-radicals*, from their property of forming salts by direct union with the metals. Each of these elements combines with an equal volume of hydrogen to form an acid which occupies the joint volumes of its constituents.

The equivalent weights of these elements also represent their atomic weights, so that they are decidedly mon-atomic elements.

The halogens also supply the most prominent example of the gradation in properties sometimes observed among the members of the same natural group of elements.

In the order of their chemical energy, that is, of the force with which they hold other elements in chemical combination with them, fluorine should stand first, its combining energy being so great as to cause a serious difficulty in isolating it at all; chlorine would rank next, then bromine, and iodine last.

The atomic weights follow the inverse order of their chemical energies:

fluorine, 19; chlorine, 35·5; bromine, 80; iodine, 127;—numbers which, of course, also represent their relative specific gravities in the state of vapour.

A similar gradation is observed in the physical state and colour of those three which are well known; chlorine being a yellow gas, bromine a red liquid, boiling at 145° F., and iodine a black solid, boiling at 347° F.

Even in the exceptions which occur to the order of chemical energy above alluded to, the same progression is noticed; thus fluorine has so little attraction for oxygen that no oxide is known, chlorine has less attraction for oxygen than bromine (chloric acid being less stable than bromic), whilst bromine has less than iodine, which is said to be capable even of uniting directly with ozonised oxygen to form iodic acid.

The compounds of these elements with hydrogen are all gases distinguished by a powerful attraction for moisture and great similarity of odour.

Their potassium-salts all crystallise in the same (cubical) form.

The fluoride of silver is deliquescent and soluble in water; the chloride is insoluble in water, but dissolves very easily in ammonia; the bromide dissolves with some difficulty in ammonia; and the iodide is insoluble.

SULPHUR.

S = 32 parts by weight = 1 volume (at 1900° F.)

137. Sulphur is remarkable for its abundant occurrence in nature in the uncombined state, in many volcanic districts. It is also found, as sulphuretted hydrogen, in many mineral waters, and very abundantly in combination with metals, forming the numerous ores known as *sulphurets* or *sulphides*, of which the following are the most abundant:—

Iron pyrites,	Bisulphide of iron,	FeS_2
Copper pyrites,	Sulphide of iron and copper,	$Cu_2S.Fe_2S_3$
Galena,	Sulphide of lead,	PbS
Blende,	Sulphide of zinc,	ZnS
Crude antimony,	Sulphide of antimony,	Sb_2S_3
Cinnabar,	Sulphide of mercury,	HgS.

Sulphur is plentifully distributed also, in combination with oxygen and a metal, in the form of *sulphates*, of which the most conspicuous are:—

Gypsum,	Sulphate of lime,	$CaO.SO_3.2H_2O$
Heavy spar,	Sulphate of baryta,	$BaO.SO_3$
Celestine,	Sulphate of strontia,	$SrO.SO_3$
Epsom salts,	Sulphate of magnesia,	$MgO.SO_3.7H_2O$
Glauber's salt,	Sulphate of soda,	$Na_2O.SO_3.10H_2O$.

In plants, sulphur is also found in the form of sulphates, and as a constituent of the vegetable albumen (of which it forms about 1·5 per cent.) present in the sap. It is also contained in certain of the essential oils remarkable for their peculiar pungent odour, such as—

Essence of garlic,	$C_6H_{10}S$.
Essence of mustard,	C_4H_5NS.

In animals, sulphur occurs as sulphates, as a constituent of albumen, fibrine, and caseine (in neither of which does it exceed 2 per cent.); and in bile, one of the products from which (taurine, $C_2H_7NO_3S$) contains 25 per cent. of sulphur.

For our supplies of sulphur we are chiefly indebted to Sicily, where large quantities of it are found in an uncombined state in beds of blue

clay. Magnificent crystalline masses of sulphate of strontia are often found associated with it; the sulphur itself sometimes occurs in the form of transparent yellow octahedra, but more frequently in opaque amorphous masses. The districts in which sulphur is found are usually volcanic, and those which border the Mediterranean are particularly rich in it. Sulphur has also been found in Iceland and California.

The *native* sulphur being commonly distributed in veins through masses of gypsum and celestine, has to be separated from these by the action of heat. When the ores contain more than 12 per cent. of sulphur, the bulk of it is melted out, the ore being thrown into rough furnaces or cauldrons with a little fuel, and smothered up with earth, so as to prevent the combustion of the sulphur, which runs down in the liquid state to the bottom of the cauldron, and is drawn out into wooden moulds.* But when the proportion of sulphur is small, the ore is heated so as to convert the sulphur into vapour, which is condensed in another vessel. The operation is conducted in Sicily in rows of earthen jars (A, fig. 195), heated in a long furnace,

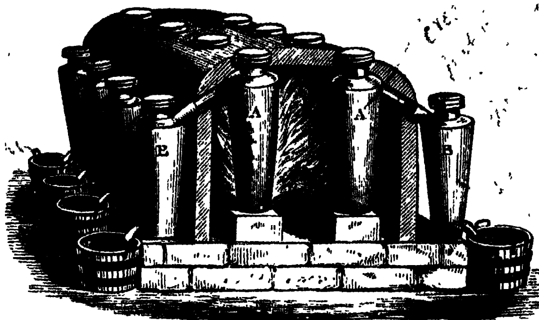


Fig. 195.—Distillation of sulphur.

and provided with short lateral pipes, which convey the sulphur into similar jars (B) standing outside the furnace, in which the vapour of sulphur condenses in the liquid state, and flows out into pails of water. The sulphur obtained by this process is imported as *rough sulphur*, and con-

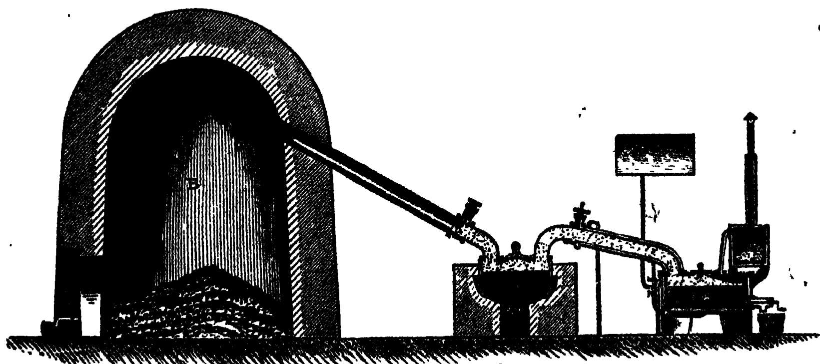


Fig. 196.—Sulphur refinery.

tains 3 or 4 per cent. of earthy impurities. In order to separate these it is redistilled, in this country, in an iron retort (A, fig. 196), from which

* High pressure steam has been applied with advantage for melting the sulphur out of the ores, which are enclosed in an iron vessel.

the vapour is conducted into a large brick chamber (B), upon the sides of which it is deposited in the form of a pale yellow powder (*flowers of sulphur*, or *sublimed sulphur*). When the operation has been continued for some time the walls of the chamber become sufficiently hot to melt the sulphur, which is allowed to collect, and afterwards cast in wooden moulds, forming *roll sulphur* or *brimstone*. *Distilled sulphur* is obtained by allowing the vapour to pass from the retort into a small receiving-vessel (C) cooled by water, where it condenses in the liquid state; this variety of sulphur is preferred for the manufacture of gunpowder, for reasons which will be stated hereafter.

Sulphur is readily distilled on a small scale in a Florence flask (fig. 197), another flask cut off at the neck (see p. 171) being employed as a receiver. The flask containing the sulphur should be supported upon a thin iron wire triangle, and heated by a gauze-burner, at first gently, and afterwards to the full heat. Flowers of sulphur will at first condense in the receiver, and will be followed by distilled sulphur when the temperature increases. A slight explosion of the mixture of sulphur vapour and air may take place at the commencement of the distillation. An ounce of sulphur may be distilled in a few minutes.

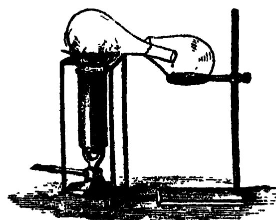
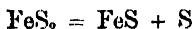


Fig. 197.—Distillation of sulphur.

We are by no means entirely dependent upon Sicily for sulphur, for this element can be easily extracted from iron and copper pyrites, both which are found abundantly in this country.

Iron pyrites forms the yellow metallic-looking substance which is often met with in masses of coal, sometimes in distinct cubical crystals, and which is to be picked up in large quantities on some sea-beaches, where it occurs in rounded nodules, rusty outside, but having a fine radiated metallic fracture. When this mineral is strongly heated it gives up part of its sulphur; at a very high temperature one half of the sulphur may be separated—



$$FeS_2 = FeS + S$$

but by an ordinary furnace heat only about one-fourth can be obtained. The distillation of iron pyrites is sometimes effected in conical fire-clay vessels (fig. 198) closed at the wider end, and stopped towards the other with a perforated plate to allow the passage of the sulphur vapour. Each vessel contains 100 lbs. of pyrites, and yields 14 lbs. of sulphur.

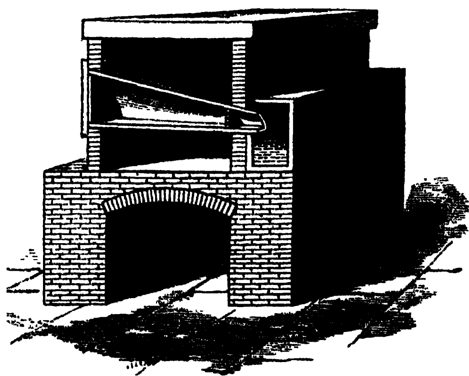


Fig. 198.—Furnace for distillation of sulphur from pyrites.

The sulphur obtained in this way has a green colour, due to the presence of a little sulphide of iron carried over mechanically during the distillation; in order to purify it, it is melted and allowed to cool slowly,

when the sulphide of iron subsides; the upper portion of the mass is then further purified by distillation.

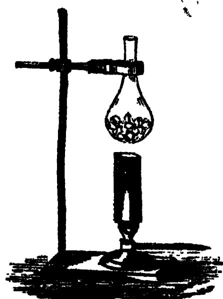
Sulphur may also be obtained from copper pyrites ($Cu_2S.Fe_2S_3$) in the process of roasting the ore previously to the extraction of the copper. The ore is heaped up into a pyramid, the base of which is about 30 feet square; a layer of powdered ore is placed at the bottom to prevent too rapid access of air; above this there is a layer of brushwood: a wooden chimney is placed in the centre, and is made to communicate with air-passages left between the faggots; around this chimney the large fragments of the ore are piled to a height of about 8 feet, and a layer of powdered ore, about 12 inches deep, is strewn over the whole. The heap contains about 2000 tons of pyrites, and will yield 20 tons of sulphur. The fire, being kindled by dropping lighted faggots down the chimney, burns very slowly because of the limited access of air, and after a few days sulphur is seen to exude from the surface, and is received in cavities made for the purpose in different parts of the heap; the roasting requires five or six months for its completion. In this operation a part of the sulphur has been separated by the mere action of heat, and another part has been displaced by the oxygen of the air, which has converted a portion of the iron into an oxide; a part of the separated sulphur has been burnt, the rest having escaped combustion on account of the limited access of air.

The sulphur extracted from pyrites is generally found to contain a little arsenic, which is frequently associated with those minerals. Immense quantities of sulphur are consumed in this country for the manufacture of sulphuric acid, gunpowder, lucifer matches, vulcanised caoutchouc, and for making the sulphurous acid employed in bleaching processes.

Much sulphur has recently been extracted from the *tank-waste* of the alkali works, by a process which will be described in the manufacture of carbonate of soda.

138. *Properties of sulphur.*—In its ordinary forms sulphur has a characteristic yellow colour, though *milk of sulphur*, or precipitated sulphur (obtained by adding an acid to the solution of sulphur in an alkali), is white. It suffers electrical disturbance with remarkable facility, so that when powdered in a dry mortar it clings to it with great pertinacity.

One of the most remarkable features of sulphur is its inflammability, due to its tendency to combine with oxygen at a moderately elevated temperature. It melts at a heat not much above the boiling point of water (239° F.), and inflames at about 500° F., burning with a pale blue flame, and emitting the well-known suffocating odour of sulphurous acid (SO_2).


Fig. 199.

The changes in the physical condition of this element under the influence of heat are very extraordinary. If a quantity of sulphur be introduced into a Florence flask and subjected to a gradually increasing heat (fig. 199), it is soon converted into a pale yellow limpid liquid (250° F.), the colour of which becomes gradually brown as the heat rises, until, at about 350° F., it is nearly black and opaque, and is so viscid that the flask may be inverted without spilling it; at this point the temperature of the sulphur remains stationary for a time, notwithstand-

ing that it is still over the flame, showing that heat is becoming latent in converting the sulphur into the new modification. On continuing the heat, the sulphur once more becomes liquid (500°), though not so mobile as at first, and at a much higher temperature (836° F.) it boils, and is converted into a brownish red very heavy vapour; at this point of the experiment, an explosion of the mixture of sulphur vapour with air often takes place. The flask may now be removed from the flame, and a little of the sulphur poured into a vessel of water, through which it will descend in a continuous stream, forming a soft elastic string like india-rubber; the portion remaining in the flask will be observed, as it cools, to pass again through the same states, becoming viscid at 350° and very liquid at 250°; another portion may now be poured into water, through which it will fall in isolated drops, solidifying into yellow brittle crystalline buttons of ordinary sulphur. As the portion of sulphur left in the flask cools, it will be found to deposit small tufts of crystals, and ultimately to solidify altogether to a yellow crystalline mass.

The brown *ductile sulphur*, when kept for a few hours, will become yellow and brittle, passing, in great measure, spontaneously into the crystalline sulphur. The change is accelerated by a gentle heat, and is attended with evolution of the heat which the sulphur was found to absorb at 350° F. Both these varieties of sulphur are, of course, insoluble in water, and they are not dissolved to any great extent by alcohol and ether. If the crystalline variety be shaken with a little bisulphide of carbon it rapidly dissolves, and on allowing the solution to evaporate spontaneously, it deposits beautiful octahedral crystals, resembling those of native sulphur (fig. 200). Ductile sulphur, however, is insoluble in bisulphide of carbon.

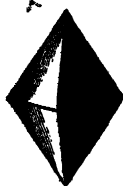
When flowers of sulphur are shaken with bisulphide of carbon, a considerable quantity passes into solution, the remainder consisting of the *amorphous*, or insoluble sulphur. Roll sulphur dissolves to a greater extent, and sometimes entirely, in the bisulphide, and distilled sulphur is always easily soluble.

The soluble and insoluble forms of sulphur appear to represent distinct chemical varieties of the element. When a solution of sulphuretted hydrogen (H_2S) is decomposed by the galvanic battery, the hydrogen, as would be expected, is separated at the negative pole, and the sulphur at the positive pole (page 5). The sulphur, therefore, was the *electronegative* element of the compound. This sulphur is soluble in bisulphide of carbon. When an acid is added to a solution of an alkaline sulphide containing more than one equivalent of sulphur, the excess of the latter is precipitated, and is then also found to be soluble in bisulphide of carbon, for it played an electronegative part towards the metal with which it was in combination.

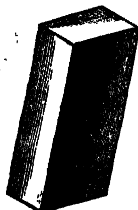
When sulphurous acid (SO_2) is decomposed by the battery, the sulphur is separated at the negative pole, showing that it played an *electropositive* part in the sulphurous acid. This electropositive sulphur is insoluble in bisulphide of carbon. The sulphur in the chloride of sulphur (S_2Cl_2) also plays an electropositive part, and accordingly, when this compound is decomposed by water, the sulphur which separates is insoluble in bisulphide of carbon. The existence of these two forms of sulphur affords some support to the theory of the dual constitution of the elements noticed at page 52.

The electropositive sulphur would be expected to manifest a greater attraction for oxygen than the electronegative variety, and accordingly, it

is found to be far more easily oxidised by nitric acid. Electropositive or insoluble sulphur is converted into electronegative or soluble sulphur by the action of a moderate heat, itself evolving heat during the process of conversion. When melted in contact with sulphurous acid, the soluble sulphur is converted externally into the insoluble form.


Fig. 200.

Crystalline or soluble sulphur is capable of existing in two distinct forms. The natural form of crystallised sulphur is the octahedron with a rhombic base (fig. 200), and this is the usual form which sulphur assumes when crystallised from its solutions. But if sulphur be melted in a covered crucible, allowed to cool until the surface has congealed, and the remaining liquid portion poured out after piercing the crust (with two holes, one for admission of air), the crucible will be lined with beautiful needles which are oblique prisms (fig. 201). These crystals are brownish yellow, and transparent when freshly made; but they soon become opaque yellow, and although they retain their prismatic appearance, they have now changed into minute rhombic octahedra, the change being attended with evolution of heat. On the other hand, if a crystal of octahedral sulphur be exposed for a short time to a temperature of about 230° F. (in a boiling saturated solution of common salt, for example), it becomes opaque, in consequence of the formation of a number of minute prismatic crystals in the mass.


Fig. 201.

The difference between these two forms of crystalline sulphur extends to their fusing-points and specific gravities; the prismatic sulphur fusing at 248° F., and the octahedral sulphur at 239° F.; the specific gravity of the prisms being 1·98, and that of the octahedra 2·05.

Roll sulphur, when freshly made, consists of a mass of oblique prismatic crystals, but after being kept for some time, it consists of octahedra, although the mass generally retains the specific gravity proper to the prismatic form. This change in the structure of the mass, taking place when its solid condition prevented the free movement of the particles, gives rise to a state of tension which may account for the extreme brittleness of roll sulphur. If a stick of sulphur be held in the warm hand, it often splits, from unequal expansion. These peculiarities of sulphur deserve careful study, as helping to elucidate the spontaneous alterations in the structure of glass, iron, &c., under certain conditions.

Flowers of sulphur do not present a crystalline structure, but consist of spherical granules composed of insoluble sulphur enclosing soluble sulphur. Hot oil of turpentine dissolves sulphur freely, and when the solution is allowed to stand, the crystals which are deposited whilst the solution is hot, have the prismatic form, but as it cools, octahedra are separated.

The following table exhibits the chief *allotropic* forms of sulphur :—

	Sp. gr.	Fusing point.	
Octahedral . . . Electro negative .	2·05	239°	Soluble in bisulphide of carbon.
Prismatic . . .	1·98	248°	Soluble in bisulphide of carbon.
Ductile . . . . Amorphous . . . Electropositive . .	1·96	Becomes octahedral.	Insoluble in bisulphide of carbon.

The octahedral is by far the most stable of the three, and is the ultimate condition which the others assume.

Other varieties of sulphur, such as a black and a red modification, have been described, but they are of minor importance.

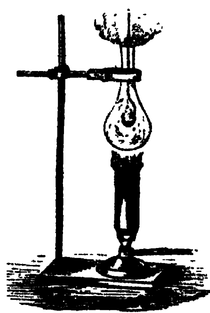
Sulphur is capable of entering into direct combination with several other elements. It unites with chlorine and with some of the metals, if finely divided, even at the ordinary temperature, and it is capable of combining at a high temperature with all the non-metals except nitrogen, and with nearly all the metals.

If a mixture of 2 parts of copper filings and 1 part of sulphur, or of equal weights of iron filings and sulphur, be heated in a Florence flask or a test-tube, the combination will be attended with vivid combustion.

The so-called *Lemery's volcano* was made by mixing iron filings with two-thirds of their weight of powdered sulphur, and burying several pounds of the moist mixture in the earth, when the heat evolved by the rusting of part of the iron provoked the energetic combination of the remainder with the sulphur, and the consequent development of much steam.*

Several metals may be made to burn in sulphur vapour, as in oxygen, by heating the sulphur in a Florence flask with a gauze burner so as to keep the flask constantly filled with the brown vapour. Potassium and sodium, introduced in deflagrating spoons, take fire spontaneously in the vapour (fig. 202).

A coil of copper wire glows vividly in sulphur vapour, and becomes converted into a brittle mass of sulphide of copper.


Fig. 202.

Sulphur dissolves, though slowly, in boiling concentrated nitric and sulphuric acids, being oxidised by the former into sulphuric, and by the latter into sulphurous acid. It is far more rapidly converted into sulphuric acid by a mixture of nitric acid and chlorate of potash. The alkalies dissolve sulphur when heated, yielding yellow or red solutions which contain hyposulphites of the alkalies and sulphides of their metals.

There is a very general resemblance in composition between the compounds of sulphur and those of oxygen with the same elements.

139. *Influence of temperature upon the specific gravity of gases and vapours.*—The specific gravity of a gas or vapour being defined as its weight, compared with that of an equal volume of dry and pure air at the same temperature and pressure, it might be supposed that so long as the temperatures were equal, their actual thermometric value would not influence the specific gravity. Indeed, with those gases and vapours which are condensible with difficulty, this is actually the case. Thus, if equal volumes of oxygen and air be weighed, either at a low or a high temperature, provided their temperatures are the same, their weights will always stand to each other in the ratio of 1·1057 : 1.

But with many vapours it is found that if they be weighed at temperatures too nearly approaching to their condensing points, their specific gravities are much higher than they are found to be at higher tempera-

* A mixture of 60 parts of fine iron filings, 2 of sal-ammoniac, and 1 of sulphur, made into a paste with water, is very useful for making the joints of iron tubes air-tight, for it sets into a hard cement, the iron combining with the sulphur.

tures. Sulphur affords a very well-marked instance of this. It boils at 836° F., and if its vapour be weighed at a temperature of 900° F., it is found to weigh 6·617 times as much as an equal volume of air at 900° F., so that it is 96 times as heavy as hydrogen, or 1 atom of sulphur would occupy $\frac{1}{3}$ vol. But if the vapour of sulphur be weighed at 1900° F., it is found to weigh only 2·23 times as much as an equal volume of air at the same temperature and pressure, so that it is only 32 times as heavy as hydrogen, and one atom of sulphur occupies 1 vol.

Hydrosulphuric Acid.

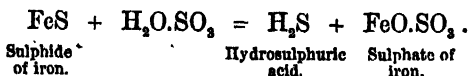
H_2S = 34 parts by weight = 2 vols.

140. *Sulphuretted hydrogen*, or hydrosulphuric acid, has been already mentioned as occurring in some mineral waters, as at Harrowgate. It is also found in the gases emanating from volcanoes, sometimes amounting to one-fourth of their volume. It is a product of the putrefaction of organic substances containing sulphur, and is one of the causes of the sickening smell of drains, &c. Eggs, which contain a considerable proportion of sulphur, evolve sulphuretted hydrogen as soon as they begin to change, and hence the association between this gas and the "smell of rotten eggs." The same smell is observed when a kettle boils over upon a coke or coal fire, the hydrogen liberated from the water combining with the sulphur present in the fuel.

Hydrosulphuric acid is also found among the products of destructive distillation of organic substances containing sulphur; it was mentioned among the products from coal, in which it is for the most part combined with the ammonia formed at the same time, producing hydrosulphate of ammonia.

It may be produced, though not in large quantity, by the direct union of hydrogen with sulphur vapour at a high temperature, or by passing a mixture of sulphur vapour and steam through a tube filled with red-hot pumice stone (the latter encouraging the action by its porosity). Hydrosulphuric acid is more readily formed by heating a damp mixture of sulphur and wood charcoal, and may be obtained in large quantity by heating a mixture of equal weights of sulphur and tallow, the latter furnishing the hydrogen.

Preparation of hydrosulphuric acid.—For use in the laboratory, where it is very largely employed in testing for and separating metals, hydrosulphuric acid is generally prepared by decomposing sulphide of iron with diluted sulphuric acid—



$$FeS + H_2O.SO_3 = H_2S + FeO.SO_3.$$

Sulphide of iron. Hydrosulphuric acid. Sulphate of iron.

To obtain sulphide of iron, a mixture of 3 parts of iron filings with 2 parts of flowers of sulphur is thrown, by small portions at a time, into an earthen crucible (A, fig. 203), heated to redness in a charcoal fire, the crucible being covered after each portion has been added. The iron and sulphur combine with combustion, and when the whole of the mixture has been introduced, the crucible is allowed to cool, the mass of sulphide of iron broken out, and a few fragments of it are introduced into a bottle (fig. 204) provided with a funnel tube for the addition of the acid, and a bent tube for conducting the gas through a small quantity of water, to remove any splashes of sulphate of iron. From the second bottle the gas is conducted by a glass

tube with a caoutchouc joint, either down into a gas-bottle, or into water, or any other liquid upon which the gas is intended to act. The fragments of sulphide of iron should be covered with enough water to fill the gas-bottle to about one-third, and strong sulphuric acid added by degrees through the funnel, the bottle being shaken, until effervescence is observed. An excess of strong sulphuric acid stops the evolution of gas by precipitating a quantity of white anhydrous sulphate of iron, which coats the sulphide and defends it from the action of the acid. When no more gas is required, the acid liquid should be at once poured away, leaving the fragments of sulphide of iron at the bottom of the bottle for a fresh operation. The liquid, if set aside, will deposit beautiful green crystals of *copperas* or sulphate of iron ($FeO.SO_3.7H_2O$).

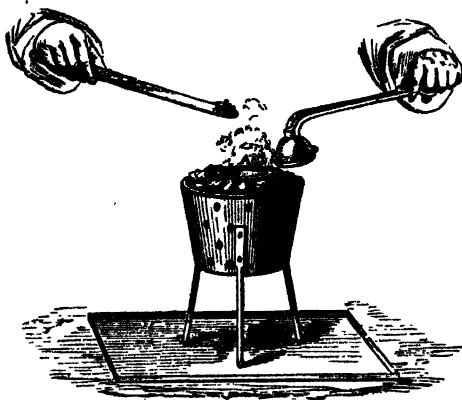
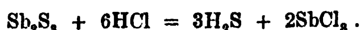


Fig. 203.

Since the sulphide of iron prepared as above generally contains a little metallic iron, the sulphuretted hydrogen is mixed with free hydrogen, which does not generally interfere with its uses. The pure gas may be prepared by heating sulphide of antimony (crude antimony) in a flask with hydrochloric acid—



$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3 .$$

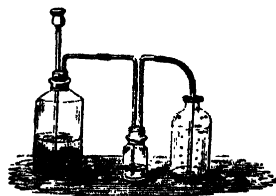
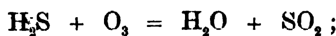


Fig. 204.—Preparation of hydrosulphuric acid.

Properties of hydrosulphuric acid.—This gas is at once distinguished from all others by its disgusting odour. It is one-fifth heavier than air (sp. gr. 1·1912). Its gaseous state is not permanent, but a pressure of 17 atmospheres is required to reduce it to a colourless liquid which congeals to a transparent solid at − 122° F. Water absorbs about three times its volume of sulphuretted hydrogen at the ordinary temperature; both the gas and its solution are feebly acid to blue litmus paper. The gas is very combustible, burning with a blue flame like that of sulphur, and yielding, as the chief products, water and sulphurous acid—



$$H_2S + O_3 = H_2O + SO_2 ;$$

a little hydrated sulphuric acid ($H_2O.SO_3$) is also formed, and unless the supply of air is very good, some of the sulphur will be separated; thus, if a taper be applied to a bottle filled with sulphuretted hydrogen, a good deal of sulphur will be deposited upon the sides. This combustibility of sulphuretted hydrogen is of the greatest importance in those processes of chemical manufacture in which this gas is evolved (as in the preparation of ammoniacal salts from gas liquors), enabling it to be disposed of in the furnace instead of becoming a nuisance to the neighbourhood. The gas causes fainting when inhaled in large quantity, and appears much to depress the vital energy when breathed for any length of time even in a diluted state.

When dissolved in water, hydrosulphuric acid is slowly acted upon by the oxygen of the air, which converts its hydrogen into water, and causes a white deposit of (electronegative or soluble) sulphur.

This is a great drawback to the use of this indispensable chemical in the laboratory, since the solution of hydrosulphuric acid is so soon rendered useless. To diminish it as far as possible, the solution should be made either with boiled water (free from dissolved air), or with water which has already been once charged with the gas and spoilt by keeping, for all the oxygen dissolved in this water will have been consumed by the former portion of gas. The gas should be passed through the water until, on closing the bottle with the hand and shaking violently, the pressure is found to act outwards, showing the water to be saturated with the gas. By closing the bottle with a greased stopper, and inverting it, the solution may be preserved for some weeks, even though occasionally opened for use.

In preparing the solution of hydrosulphuric acid, a certain quantity of the gas always escapes absorption. To prevent this from becoming a nuisance, the bottle containing the water to be charged with gas may be covered with an air-tight caoutchouc cap having two tubes, through one of which passes the glass tube conveying the gas down into the water, and through the other, a tube conducting the excess of gas either into a gas-burner, where it may be consumed, or into a solution of ammonia which will absorb it, forming the very useful hydrosulphate of ammonia.

The hydrogen of the hydrosulphuric acid is oxidised immediately by nitrous acid (N_2O_3), the sulphur being separated, and a considerable quantity of nitrite of ammonia produced—

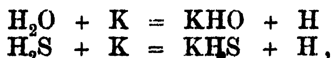


$$N_2O_3 + 6H_2S = 2NH_3 + 3H_2O + S_6.$$

Concentrated nitric acid also oxidises the hydrogen and a part of the sulphur, sulphate of ammonia ($2NH_3.H_2O.SO_3$) being found in the solution, and a pasty mass of sulphur separated. Chlorine, bromine, and iodine at once appropriate its hydrogen and separate the sulphur.

In its action upon the metals and their oxides, hydrosulphuric acid resembles hydrochloric and the other hydrogen acids. Many of the metals displace the hydrogen and form metallic sulphides. This usually requires the assistance of heat, but mercury and silver act upon the gas at the ordinary temperature. Thus, if sulphuretted hydrogen be collected over mercury, the surface of the latter becomes coated with a black film of sulphide of mercury; $H_2S + Hg_2 = H_2 + Hg_2S$. In a similar way the surface of silver is slowly tarnished when exposed to sulphuretted hydrogen, its surface being covered with a black film of sulphide of silver. It is on this account that silver plate is so easily blackened by the air of towns, which is contaminated with sulphuretted hydrogen. An egg spoon is always blackened by the sulphur from the egg. Silver coins kept in the pocket with lucifer matches are blackened, from the formation of a little sulphide of silver. The original brightness of the coin may be restored by rubbing it with a solution of cyanide of potassium, which dissolves the sulphide of silver. Friction with strong ammonia will also remove the tarnish, and its application is safer than that of the poisonous cyanide.

When heated in the gas, several metals displace the hydrogen from it. Thus, potassium acts upon it in a corresponding manner to that in which it acts upon water—



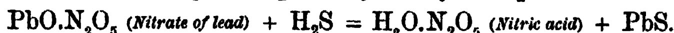
$$H_2O + K = KHO + H$$
$$H_2S + K = KHS + H,$$

forming *hydrosulphate of potassium* (KHS).

Tin removes the whole of the sulphur from hydrosulphuric acid at a moderate heat; $Sn + H_2S = H_2 + SnS$.

When hydrosulphuric acid acts upon a metallic oxide, it generally converts it into a sulphide corresponding to the oxide, whilst the hydrogen

and oxygen unite to form water. Oxide of lead in contact with the gas yields black sulphide of lead and water; $PbO + H_2S = PbS + H_2O$. Even if the oxide of lead be combined with an acid, the same change is produced by hydrosulphuric acid; and hence paper impregnated with a salt of lead is used as a test for the presence of this gas. Thus, if paper be spotted with a solution of nitrate (or acetate) of lead, it will indicate the presence of even minute quantities of sulphuretted hydrogen (in impure coal-gas, for example) by the brown colour imparted to the spots, the nitrate of lead being decomposed by the hydrosulphuric acid—



$$PbO.N_2O_5 \text{ (Nitrate of lead)} + H_2S = H_2O.N_2O_5 \text{ (Nitric acid)} + PbS.$$

It is in this manner that paints containing white lead (carbonate of lead) are darkened by exposure to the air of towns. Cards glazed with white lead, and engravings on paper whitened with that substance, suffer a similar change. Paintings, whether in oil or water colours, in which lead is an ingredient, are also injured by air containing sulphuretted hydrogen. The interesting observation has recently been made that such colours, damaged by the formation of sulphide of lead, are restored by the continued action of light and air, the black sulphide of lead becoming oxidised and converted into the white sulphate of lead, $PbS + O_4 = PbO.SO_3$. In the dark this restoration does not take place, so that it is often a mistake to screen pictures from the light by a curtain.

The action of hydrosulphuric acid upon the chlorides and other haloid salts of the metals generally resembles its action upon the oxides of the same metals.

Most of the sulphides of the metals, like the corresponding oxides, are insoluble in water, but many of the sulphides are also insoluble in diluted acids and in alkalies, so that when hydrosulphuric acid is brought into contact with the solutions of metals, it will often precipitate the metal in the form of a sulphide having some characteristic colour or other property by which the metal may be identified.

Any solution of lead will give a *black* precipitate with solution of hydrosulphuric acid, the sulphide of lead being insoluble in diluted acids and in alkalies.

A solution of antimony (tartar-emetic, for example, the tartrate of antimony and potash) mixed with an excess of hydrochloric acid, gives an *orange*-coloured precipitate (Sb_2S_3) on adding hydrosulphuric acid; but if another portion be mixed with an excess of potash before adding the hydrosulphuric acid, there will be no precipitate, for the sulphide of antimony is soluble in alkalies.

Chloride of cadmium gives a brilliant *yellow* precipitate of sulphide of cadmium on adding hydrosulphuric acid.

Sulphate of zinc yields a *white* precipitate of sulphide of zinc (ZnS), but if a little hydrochloric acid be previously added, no precipitate is formed, the sulphide of zinc being soluble in acids. On neutralising the hydrochloric acid with ammonia, the sulphide of zinc is at once precipitated.

It is evident that, in a solution containing cadmium and zinc, the metals may be separated by acidifying the liquid with hydrochloric acid, and adding excess of hydrosulphuric acid, which precipitates the sulphide of cadmium only. On filtering the solution, and adding ammonia, the sulphide of zinc is precipitated.

Sulphur-acids and *sulphur-bases*.—Those sulphides which are soluble in the alkalies are often designated sulphur-acids, whilst the sulphides of the alkali-metals are sulphur-bases. These two classes of sulphides combine to form *sulphur-salts* analogous in composition to the oxygen-salts of the same metals. Thus, there have been crystallised, the salts

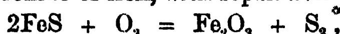
Sulphostannate of (sulphide of)	sodium,	$2Na_2S.SnS_2$
Sulphantimoniate	,,	,,	$3Na_2S.Sb_2S_5$
Sulpharseniate	,,	,,	$3Na_2S.As_2S_5$.

The sulphostannic (SnS_3), sulphantimonic (Sb_2S_5), and sulpharsenic (As_2S_5) acids respectively, corresponding to stannic (SnO_2), antimonic (Sb_2O_5), and arsenic (As_2O_5) acids.

The *action of air upon the sulphides* of the metals is often turned to account in chemical manufactures. At the ordinary temperature, the sulphides of those metals which form alkaline oxides (such as sodium and calcium), when exposed to the air in the presence of water, yield, first, mixtures of the oxide and bisulphide, $2Na_2S + O = Na_2O + Na_2S_2$; and afterwards the hyposulphite, $Na_2S_2 + O_3 = Na_2S_2O_3$. This change is sometimes turned to account for the manufacture of hyposulphite of soda.

When the metal forms a less powerful base with oxygen, the sulphide is often converted into sulphate by exposure to moist air; thus, $CuS + O_4 = CuO.SO_3$, which is taken advantage of for the separation of copper from tin ores.

The black sulphide of iron (FeS), when exposed to moist air, becomes converted into red peroxide of iron, with separation of sulphur—



$$2FeS + O_3 = Fe_2O_3 + S_2,$$

a change which enables the gas manufacturer to revive, by the action of air, the peroxide of iron employed for removing the sulphuretted hydrogen from coal gas.

When *roasted* in air at a high temperature, the sulphides corresponding to the more powerful bases are converted into sulphates; thus $ZnS + O_4 = ZnO.SO_3$, which explains the production of sulphate of zinc by roasting blende. But in most cases part of the sulphur is converted into sulphurous acid at the same time. Subsulphide of copper, for instance, is partly converted into oxide of copper by roasting, $Cu_2S + O_4 = 2CuO + SO_2$, a change of great importance in the extraction of copper from its ores.

141. *Persulphide of hydrogen.*—The composition of this substance is not yet satisfactorily ascertained. The similarity of its chemical properties to those of binoxide of hydrogen prompts the wish that its formula may be H_2S_2. Some analyses, however, seem to lead to the formula H_2S_5, but since the persulphide is a liquid capable of dissolving free sulphur, which is not easily separated from it, there is much difficulty in determining the exact proportion of this element with which the hydrogen is combined.

When equal weights of slaked lime and sulphur are boiled with water, an orange-coloured liquid is formed, which contains hyposulphite of lime, bisulphide of calcium, and pentasulphide of calcium (CaS_5)—



$$3CaO + S_6 = CaS_2O_3 \textit{ (Hyposulphite of lime) } + 2CaS_2 \textit{ (Bisulphide of calcium).}$$

When hydrochloric acid is added to the filtered solution, an abundant precipitation of sulphur occurs, and much hydrosulphuric acid is evolved—



$$CaS_2 + 2HCl = CaCl_2 + H_2S + S.$$

But if the solution be poured by degrees into a slightly warm mixture of hydrochloric acid with twice its bulk of water, and constantly stirred, a yellow heavy oily liquid collects at the bottom, which is the persulphide of hydrogen—



$$CaS_2 + 2HCl = H_2S_2 (?) + CaCl_2.$$

The acid having been kept in excess, the persulphide has been preserved from the decomposition which it suffered in the presence of the alkaline solution in the former experiment. For the persulphide of hydrogen very closely resembles the peroxide in the facility with which it may be decomposed into hydrosulphuric acid and sulphur; it undergoes spontaneous decomposition even in sealed tubes, and the hydrosulphuric acid then becomes liquefied by its own pressure. Most of the substances, the contact of which promotes the decomposition of the peroxide of hydrogen, have the same effect upon the persulphide. This compound has a peculiar odour which appears to affect the eyes; of course, its vapour is mixed with that of hydrosulphuric acid resulting from its decomposition.

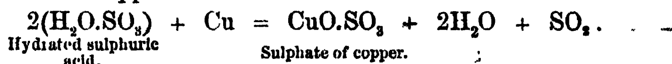
Oxides of Sulphur.

142. Only two compounds of sulphur with oxygen have been obtained in the separate state, viz., *sulphurous acid* (SO_2) and *sulphuric acid* (SO_3).

Sulphurous Acid.

SO_2 = 64 parts by weight = 2 vols.

143. In nature, sulphurous acid is but rarely met with; it exists in the gases issuing from volcanoes. Although constantly discharged into the air of towns by the combustion of coal (containing sulphur), it is so easily oxidised and converted into sulphuric acid, that no considerable quantity is ever found in the atmosphere. Sulphurous acid has been already mentioned as the sole product of the combustion of sulphur in dry air and oxygen, but it is generally prepared for chemical purposes by removing part of the oxygen from sulphuric acid, which is easily effected by heating it with metallic copper—



$$\underset{\text{Hydrated sulphuric acid.}}{2(H_2O.SO_3)} + Cu = \underset{\text{Sulphate of copper.}}{CuO.SO_3} + 2H_2O + SO_2.$$

300 grains of copper clippings are heated in a Florence flask with 4 oz. (measured) of strong sulphuric acid, the gas being conducted by a bent tube down to the bottom of a dry bottle closed with a perforated card (see fig. 177, p. 153). Some time will elapse before the gas is evolved, for sulphuric acid acts upon copper only at a high temperature; but when the evolution of gas fairly commences, it will proceed very rapidly, so that it is necessary to remove the flame from under the flask. The gas will contain a little suspended vapour of sulphuric acid, which renders it turbid.

When the operation is finished, and the flask has been allowed to cool, it will be found to contain a grey crystalline powder at the bottom of a brown liquid. The latter is the excess of sulphuric acid employed, and retains very little copper, since sulphate of copper is insoluble in strong sulphuric acid. If the liquid be poured off, and the flask filled up with water, and set aside for some time, the crystalline powder will dissolve, forming a blue solution of sulphate of copper, yielding that salt in fine prismatic crystals by evaporation and cooling. The dark powder remaining undissolved after extracting the whole of the sulphate of copper consists chiefly of sulphide of copper, the production of which is interesting, as showing how far the deoxidising effect of the copper may be carried in this experiment.

Sulphurous acid is a very heavy (sp. gr. 2·25) colourless gas, characterised by its odour of burning brimstone. It condenses to a clear liquid at 0° F. (the temperature of a mixture of ice and salt) even at the ordinary pressure of the air, and has been frozen to a colourless crystalline solid at −105° F.

The liquefaction of the gas is easily exhibited by passing it down to the bottom of a tube (A, fig. 205) closed at one end, and surrounded with a mixture of pounded ice with half its weight of salt. The tube should have been previously drawn out to a narrow neck at B, which may afterwards be sealed by the blowpipe, the lower part of the tube being still surrounded by the freezing mixture, since the liquid sulphurous acid boils at 14° F. The tube need not be very strong, for at the ordinary temperature the vapour of sulphurous acid exerts a pressure of only 2·5 atmospheres. Liquid sulphurous acid is a convenient agent for producing (by its rapid evaporation) the low temperature (−39° F.) required to effect the solidification of mercury. A small globule of this metal may readily be frozen by dropping some liquid sulphurous acid upon it in a watch-glass placed in a strong draught of air. The tube containing the sulphurous acid should be held in a woollen cloth or glove. The attractive experiment of freezing water in a red-hot crucible may also be made with the liquid acid. A platinum crucible being heated to redness, and some liquid sulphurous acid poured into it, the liquid

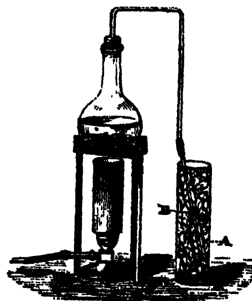


Fig. 205.

becomes surrounded with an atmosphere of sulphurous acid gas, which prevents its contact with the metal (assumes the *spheroidal* state), and its temperature is reduced by its own evaporation to so low a degree that a few drops of water allowed to flow into it will at once become converted into ice.

Sulphurous acid gas is very easily absorbed by water, as may be shown by pouring a little water into a bottle of the gas, closing the bottle with the palm of the hand, and shaking it violently (see fig. 165, p. 145), when the diminished pressure due to the absorption of the gas will cause the bottle to be sustained against the hand by the pressure of the atmosphere. Water absorbs 43·5 times its bulk of the gas at the ordinary temperature. If the solution be exposed to a low temperature, a crystallised hydrate of sulphurous acid is obtained, the composition of which does not appear to be accurately settled. When the solution of sulphurous acid is kept for some time in a bottle containing air, its smell gradually disappears, the acid absorbing oxygen and becoming converted into sulphuric acid.

Sulphurous acid, like carbonic acid, possesses in a high degree the power of extinguishing flame. A taper is at once extinguished in a bottle of the gas, even when containing a considerable proportion of air. One of the best methods of extinguishing burning soot in a chimney consists in passing up sulphurous acid by burning a few ounces of sulphur in a pan placed over the fire.

The principal uses of sulphurous acid depend upon its property of bleaching many animal and vegetable colouring matters. Although a far less powerful bleaching agent than chlorine, it is preferred for bleaching silk, straw, wool, sponge, isinglass, baskets, &c., which would be injured by the great chemical energy of chlorine. The articles to be bleached are moistened with water and suspended in a chamber in which sulphurous acid is produced by the combustion of sulphur. The colouring matters do not appear in general to be decomposed by the acid, but rather to form colourless combinations with it, for in course of time, the original colour often reappears, as is seen in straw, flannel, &c., which become yellow from age, the sulphurous acid probably being oxidised into sulphuric acid. Stains of fruit and port wine on linen are conveniently removed by solution of sulphurous acid.

The red solution obtained by boiling a few chips of logwood with river water (distilled water does not give so fine a colour), serves to illustrate the bleaching properties of sulphurous acid. A few drops of the solution of the acid will at once change the red colour of the solution to a light yellow, but that the colouring power is suspended and not destroyed, may be shown by dividing the yellow liquid into two parts, and adding to them, respectively, potash and diluted sulphuric acid, which will restore the colour in a modified form. To contrast this with the complete decomposition of the colouring matter, a little sulphurous acid may be added to a weak solution of the permanganate of potash, when the splendid red solution at once becomes perfectly colourless, and neither acid nor alkali can effect its restoration, for in this case the red permanganic acid (Mn_2O_7), supposed to exist in the permanganate of potash, is reduced to the state of protoxide of manganese.



Fig. 206.

If a bunch of damp coloured flowers be suspended in a bell-jar over a crucible containing a little burning sulphur (fig. 206), many of the flowers will be completely bleached by the sulphurous acid, and by plunging them afterwards into diluted sulphuric acid and ammonia, their colours may be partly restored, with some very curious modifications.

Another very useful property of sulphurous acid is that of arresting

fermentation (or putrefaction), apparently by killing the vegetable or animal growth which is the cause of the fermentation. This is commonly designated the *antiseptic* property of sulphurous acid, and is turned to account when casks for wine or beer are *sulphured* in order to prevent the action of any substance contained in the pores of the wood, and capable of exciting fermentation, upon the fresh liquor to be introduced. If a little solution of sugar be fermented with yeast in a flask provided with a funnel tube (fig. 207), a solution of sulphurous acid poured in through the latter will at once arrest the fermentation. The salts of sulphurous acid (sulphites) are also occasionally used to arrest fermentation, in the manufacture of sugar, for instance. Clothes are sometimes fumigated with sulphurous acid to destroy vermin, and the air of rooms is disinfected by burning sulphur in it.

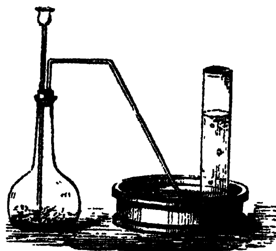


Fig. 207.

The disposition of sulphurous acid to absorb oxygen and pass into sul phuric acid, renders it a powerful deoxidising or reducing agent. Solutions of silver and gold are reduced to the metallic state by sulphurous acid if a very little ammonia be added, and a gentle heat applied.

If a solution of sulphurous acid be heated for some time in a sealed tube to 340° F. one portion of the acid deoxidises another, sulphur is separated, and sulphuric acid formed; $3SO_2 + 2H_2O = 2(H_2O.SO_3) + S$.

Sulphurous acid gas combines with ammonia gas to form two solid compounds, $(NH_3)_2SO_2$, and $NH_3.SO_2$, which are quite different in their properties from the sulphite and bisulphite of ammonia, which are formed when sulphurous acid acts upon solution of ammonia.

Chlorine combines with an equal volume of sulphurous acid, under the influence of bright sunshine, to produce a colourless liquid, the vapour of which is very acrid and irritating to the eyes. Its composition is represented by SO_2Cl_2, and it is sometimes called *chlorosulphuric acid*, though it does not combine with bases, and is decomposed by water, yielding hydrochloric and sulphuric acids. It is also known as *chloride of sulphuryle*, SO_2, being looked upon as the radical of sulphuric acid. The *chloride of thionyle*,* $SOCl_2$, is a colourless volatile liquid obtained by the action of hypochlorous acid gas on sulphur dissolved in the subchloride of sulphur. It is decomposed by water, yielding hydrochloric and sulphurous acids.

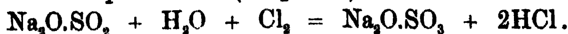
Potassium and sodium, when heated in sulphurous acid, burn vividly, producing the oxides and sulphides of the metals.

Iron, lead, tin, and zinc are also converted into oxides and sulphides when heated in sulphurous acid; $SO_2 + Zn_3 = ZnS + 2ZnO$.

Sulphites.—The acid character of sulphurous acid is rather feeble, although stronger than that of carbonic acid. There is much general resemblance between the sulphites and carbonates, in point of solubility, the sulphites of the alkali-metals being the only salts of sulphurous acid which are freely soluble in water. Sulphurous acid, like carbonic, forms two classes of salts, the sulphites (for example, sulphite of soda, $Na_2O.SO_2$) and bisulphites (as bisulphite of potash, $K_2O.H_2O.2SO_2$).

The *sulphite of soda* is extensively manufactured for the use of the papermaker, who employs it as an *antichlore* for *killing the bleach*, that is, neutralising the excess of chlorine after bleaching the rags with chloride of lime and sulphuric acid (see p. 152)—

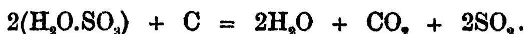
$$Na_2O.SO_2 + H_2O + Cl_2 = Na_2O.SO_3 + 2HCl.$$



* Θεῖον, *sulphur*.

It is prepared by passing sulphurous acid over damp crystals of carbonate of soda, when the carbonic acid is expelled, and sulphite of soda formed, which is dissolved in water and crystallised. It forms oblique prisms having the composition $Na_2O.SO_2.7Aq$, which effloresce in the air, becoming opaque, and slowly absorbing oxygen, passing into sulphate of soda ($Na_2O.SO_3$). Its solution is slightly alkaline to test-papers.

For the manufacture of sulphite of soda, the sulphurous acid is obtained either by the combustion of sulphur or by heating sulphuric acid with charcoal—



$$2(H_2O.SO_3) + C = 2H_2O + CO_2 + 2SO_2.$$

The carbonic acid, of course, will not interfere with this application of the sulphurous acid.

Just as in the case of carbonic acid (see p. 83), many chemists deny the acid nature of the compound SO_2 altogether, and term it *sulphurous anhydride*, reserving the name of sulphurous acid for the hydrated sulphurous acid, $H_2O.SO_2$ or H_2SO_3, obtained by exposing the aqueous solution of sulphurous acid to a very low temperature.

Sulphuric Acid.

$SO_3 = 80$ parts by weight.

144. It has been already noticed that one of the most abundant forms in which sulphur occurs in nature is that of sulphuric acid in combination with certain bases. Hydrated sulphuric acid has also been found in certain springs and rivers in volcanic regions. Sulphurous acid and oxygen gases combine to form sulphuric acid (SO_3) when passed through a tube containing heated platinum or certain metallic oxides, such as those of copper and chromium, the action of which in promoting the combination is not thoroughly understood.

The combination may be shown by passing oxygen from the tube A (fig. 208) connected with a gas-holder, through a strong solution of sulphurous acid (B), so that it may take up a quantity of that gas, afterwards through a tube (C) containing pumice stone soaked with oil of vitriol, to remove the water, and then through a bulb (D) containing platinised asbestos (see p. 138). The mixture of the gases issuing into the air is quite invisible, but when the bulb is gently heated, combination takes place, and dense white clouds are formed in the air, from the combination of the anhydrous sulphuric acid (SO_3) produced with the atmospheric moisture.

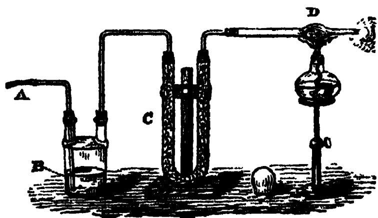


Fig. 208.

An easier method of obtaining the anhydrous sulphuric acid will be noticed hereafter, but the hydrated acid is of so much more importance that its preparation and properties should be studied before those of the anhydrous acid.

Hydrated sulphuric acid ($H_2O.SO_3 = 98$ parts by weight).—More than four centuries ago, the alchemist Basil Valentine subjected *green vitriol*, as it was then called (sulphate of iron), to distillation, and obtained an acid liquid which he named *oil of vitriol*. The process discovered by this laborious monk is even now in use at Nordhausen in Saxony, and the *Nordhausen oil of vitriol* is an important article of commerce. The crystals of sulphate of iron ($FeO.SO_3.7H_2O$) are exposed to the air so that

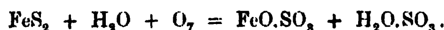
they may absorb oxygen, and become converted into the *basic persulphate of iron*—



$$2(FeO.SO_3) + O = Fe_2O_3.2SO_3.$$

This salt is dried, and distilled in earthen retorts, the oil of vitriol being condensed in receivers of glass or stoneware. The action of heat upon the basic persulphate of iron separates the acid from the base, and if the salt were absolutely dry, the anhydrous sulphuric acid would be expected to distil over. There is always enough water, however, left in the persulphate, to combine with the anhydrous acid to form the Nordhausen oil of vitriol, the composition of which is pretty correctly expressed by the formula $H_2O.2SO_3$. The peroxide of iron (Fe_2O_3) which is left in the retorts, is the red powder known as *colcothar*, which is used for polishing plate glass and metals.

The green vitriol employed for preparing the Nordhausen acid is obtained from iron pyrites (FeS_2). A particular variety of this mineral, *white pyrites* (or efflorescent pyrites), when exposed to moist air, undergoes oxidation, yielding sulphate of iron and sulphuric acid—



$$FeS_2 + H_2O + O_7 = FeO.SO_3 + H_2O.SO_3.$$

Large masses of this variety of pyrites in mineralogical cabinets may often be seen broken up into small fragments, and covered with an acid efflorescence of sulphate of iron from this cause. Ordinary iron pyrites is not oxidised by exposure to the air unless it be first subjected to distillation in order to separate a portion of the sulphur which it contains.

The Nordhausen acid is readily distinguished from English sulphuric acid by its fuming in the air when the bottle is opened. This is due to the escape of a little vapour of anhydrous sulphuric acid. It is heavier than the English acid, its specific gravity being 1·9. It is chiefly used for dissolving indigo in preparing the Saxony blue dye, and is a convenient source of the anhydrous sulphuric acid; for if it be gently heated in a retort, the anhydrous acid is disengaged, and may be condensed in silky crystals in a receiver kept cool by ice, whilst ordinary hydrated sulphuric acid ($H_2O.SO_3$) is left in the retort.

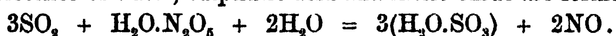
The process adopted at Nordhausen, though simple in theory, is expensive on account of the consumption of fuel and the breaking of the retorts, so that the price of the acid, compared with that of English manufacture, is very high.

The first step towards the discovery of our present process was also made by Valentine, when he prepared his *oleum sulphuris per campanum*, by burning sulphur under a bell-glass over water, and evaporating the acid liquid thus obtained. The same experimenter also made a very important advance when he burnt a mixture of sulphur, sulphide of antimony, and nitre, under a bell-glass placed over water; but it was not until the middle of the eighteenth century that it was suggested by some French chemists to burn the sulphur and nitre alone over water, a process by which the acid appears actually to have been manufactured upon a pretty large scale. The substitution of large chambers of lead for glass vessels by Dr Roebuck was a great improvement in the process, and about the year 1770 the preparation of the acid formed an important branch of manufacture; since then the process has been steadily improving, until, at the present time, upwards of 100,000 tons are annually consumed in Great Britain, and a very large quantity is exported. The diminution in the price of oil of vitriol well exhibits the progress of improvement in its production, for

the original *oil of sulphur* appears to have been sold for about half a crown an ounce, and that prepared by burning sulphur with nitre in glass vessels at the same price per pound; but when leaden chambers were introduced, the price fell to a shilling per pound, and at present oil of vitriol can be purchased at the rate of five farthings per pound.

The description of the present process of manufacture will be best understood after a consideration of the chemical changes upon which it depends.

It has been seen that when sulphur is burnt in air, sulphurous acid is the chief product. When sulphurous acid acts upon hydrated nitric acid, in the presence of water, sulphuric acid and nitric oxide are formed—



$$3SO_2 + H_2O.N_2O_5 + 2H_2O = 3(H_2O.SO_3) + 2NO.$$

Nitric oxide, in contact with air, combines with its oxygen to form nitric peroxide (NO_2).

If nitric peroxide is brought into contact with sulphurous acid and water, it is again converted into nitric oxide with formation of sulphuric acid—



$$NO_2 + SO_2 + H_2O = NO + H_2O.SO_3.$$

It appears, therefore, that nitric oxide may be employed to absorb oxygen from the air, and to convey it to the sulphurous acid, so that theoretically, an unlimited quantity of sulphurous acid, supplied with air and water, might be converted into sulphuric acid by a given quantity of nitric oxide.

To illustrate these important chemical principles of the manufacture of sulphuric acid, the following experiments may be performed:—

I. A quart bottle of nitric oxide (p. 137) is placed mouth to mouth with a pint bottle of oxygen, when both bottles will be filled with the red nitric peroxide.

II. The quart bottle of this red gas is placed mouth to mouth with a quart bottle of sulphurous acid gas (fig. 209), when the red colour will soon disappear, and the sides of the bottles will be covered with a crystalline substance formed by the reaction between the nitric peroxide, the sulphurous acid, and the small quantity of water present in the gases. The true composition of this crystalline body is doubtful, but if, for the purpose of the present reasoning, it be regarded as $2(NO.SO_3).H_2O$, its formation would be represented by the equation—



$$2NO_2 + 2SO_2 + H_2O = 2(NO.SO_3).H_2O.$$

III. A little water is shaken round the insides of the bottles, when the crystalline compound will be decomposed with effervescence, evolving nitric oxide, and producing hydrated sulphuric acid—

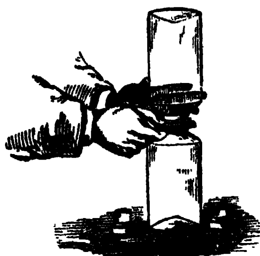
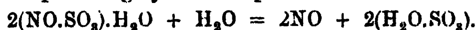


Fig. 209.



$$2(NO.SO_3).H_2O + H_2O = 2NO + 2(H_2O.SO_3).$$

IV. Air* is blown into the bottles through a glass tube, when the presence of the nitric oxide will be proved by the formation of the red nitric peroxide.

In the presence of abundance of water this crystalline compound is not produced, as may be shown by the following modification of the experiment.

V. A large glass flask or globe (A, fig. 210) is fitted with a cork, through which are passed—

(*a*) a tube connected with a flask (D) containing copper and strong sulphuric acid, for evolving sulphurous acid;

(*b*) a tube connected with a flask (B) containing copper and diluted nitric acid (sp. gr. 1·2) for supplying nitric oxide;

(*c*) a tube proceeding from a small flask (E) containing water.

* The operation is of course more striking if oxygen is employed instead of air, the globe being filled with oxygen by displacement at the commencement.

On applying a gentle heat to the flask containing nitric acid and copper, the nitric oxide passes into the globe and combines with the oxygen of the air, filling the globe with red nitric peroxide. The nitric oxide flask may then be removed. Sulphuric acid is then generated by heating the flask containing sulphuric acid and copper; the sulphurous acid will soon decolorise the red nitric peroxide, the contents of the globe becoming colourless, and the crystalline compound forming abundantly on the sides; the sulphurous acid flask may then be removed. Steam is sent into the globe from the flask containing water, when the crystalline compound will be dissolved, and sulphuric acid will collect at the bottom of the globe. If air be now blown into the globe, the nitric oxide will again acquire the red colour of nitric peroxide.

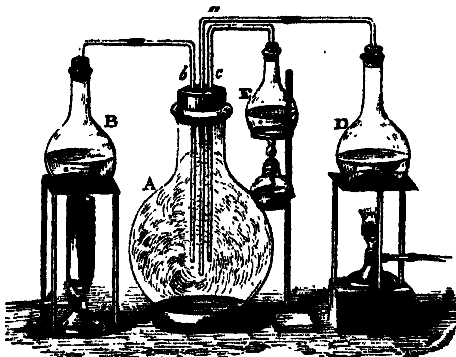


Fig. 210.—Preparation of sulphuric acid.

If the experiment be repeated, the steam being introduced simultaneously with the sulphurous acid, no crystalline compound whatever will be formed, the sulphurous acid being at once converted into hydrated sulphuric acid.

Since the cork is somewhat corroded in this experiment, it is preferable to have the mouth of the flask ground and closed by a ground glass plate, perforated with holes for the passage of the tubes. The perforations are easily made by placing the glass plate flat against the wall and piercing it with the point of a revolving rat's-tail file dipped in turpentine; the file is then gradually worked through the hole until the latter is of the required size.

The process employed for the manufacture of English oil of vitriol will now be easily understood.

A series of chambers is constructed of leaden plates, the edges of which are united by autogenous soldering (that is, by fusing their edges, without solder, which would be rapidly corroded by the acid vapours); the leaden chambers are supported and strengthened by a framework of timber (fig. 211).

The *sulphurous acid* is generated by burning sulphur or iron pyrites in a suitable furnace (A) adjoining the chambers, and so arranged that the sulphurous acid produced may be mixed with about the proper quantity of *air* to furnish the oxygen required for its conversion into sulphuric acid.

Nitric acid vapour is evolved from a mixture of nitrate of soda and oil of vitriol (see p. 131) contained in an iron pan which is heated by the combustion of the sulphur, so that the nitric acid is carried into the chambers with the current of sulphurous acid and air.

Water covers the floor of the chambers to the depth of about two inches, and jets of steam are introduced at different parts from an adjacent boiler (B).

The sulphurous acid acts upon the nitric acid vapour, in the presence of the water, forming nitric oxide and hydrated sulphuric acid, which rains down into the water on the floor of the chambers—



$$3SO_2 + H_2O.N_2O_5 + 2H_2O = 2NO + 3(H_2O.SO_3).$$

If this nitric oxide were permitted to escape from the chambers, and a fresh quantity of nitric acid vapour introduced to oxidise another portion of sulphurous acid, it is evident that 2 molecules (170 parts by weight) of

nitrate of soda would be required to furnish the nitric acid for the conversion of 3 atoms (96 parts by weight) of sulphur, whereas, in practice, 6 parts by weight only of nitrate of soda are employed for 96 parts of sulphur.

For the nitric oxide (NO) at once acquires oxygen from the air admitted together with the sulphurous acid, and becomes nitric peroxide (NO_2), which oxidises more sulphurous acid in the presence of water, converting it into hydrated sulphuric acid—



$$2SO_2 + 2NO_2 + 2H_2O = 2(HO.SO_3) + 2NO.$$

A great reduction in the volume of the gas in the chamber thus takes place (4 vols. SO_2 and 4 vols. NO_2 yielding 4 vols. NO), so that there

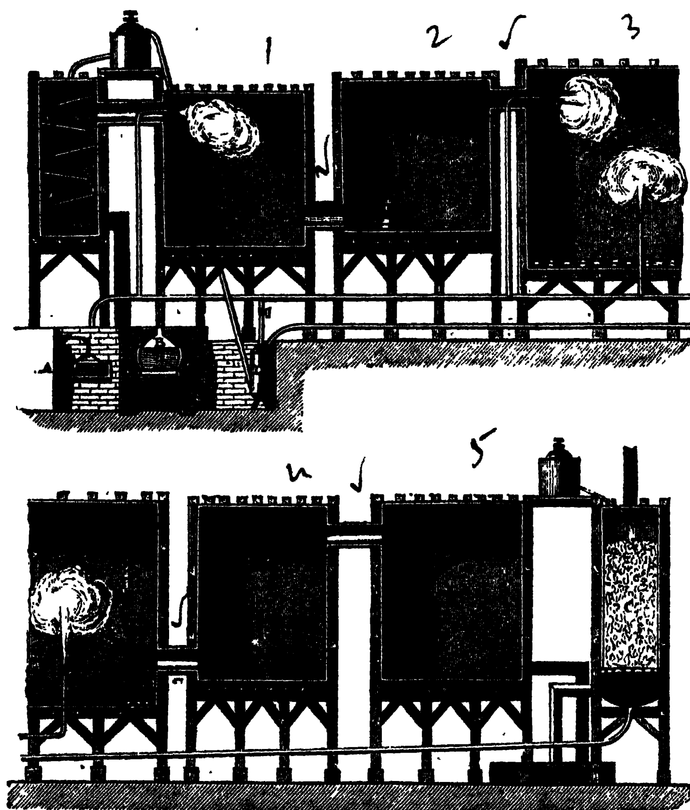


Fig. 211.—Sulphuric acid chambers.

is room for the introduction of a fresh quantity of the mixture of sulphurous acid and air from the furnace, upon which thenitric oxide acts as before, taking up the oxygen from the air and handing it over to the sulphurous acid, in the presence of water, to produce a fresh supply of hydrated sulphuric acid.

But the nitrogen of the air takes no part in these changes, and since the oxygen consumed in converting the sulphur into sulphuric acid is accompanied by four times its volume of nitrogen, a very large accumula-

tion of this gas takes place in the chambers, and provision must be made for its removal in order to allow space for those gases which take part in the change. The obvious plan would appear to be the erection of a simple chimney for the escape of the nitrogen at the opposite end of the chamber to that at which the sulphurous acid and air enter it; and this plan was formerly adopted, but the nitrogen carries off with it a portion of the nitric oxide which is so valuable in the chamber, and to save this the escaping nitrogen is now generally passed through a leaden chamber (C) filled with coke, over which oil of vitriol is allowed to trickle; the oil of vitriol absorbs the nitric oxide, and flows into a cistern (D), from which it is pumped up to the top of another chamber (E) filled with coke, or arranged with shelves in cascade, through which the hot sulphurous acid and air are made to pass as they enter, when they take up the nitric oxide from the oil of vitriol, and carry it with them into the chamber.

Before the introduction of this plan of retaining the nitric oxide by oil of vitriol, it required a quantity of nitrate of soda amounting to $\frac{1}{8}$th or $\frac{1}{12}$th of the weight of the sulphur to convert it into sulphuric acid, whereas about $\frac{1}{20}$th or even less is now often made to suffice.

The sulphuric acid is allowed to collect on the floor of the chamber until it has a specific gravity of about 1·6, and contains 70 per cent. of oil of vitriol ($H_2O.SO_3$). If it were allowed to become more concentrated than this, it would absorb some of the nitric oxide in the chamber, so that it is now drawn off.

This acid is quite strong enough for some of the applications of sulphuric acid, particularly for that which consumes the largest quantity in this country, viz., the conversion of common salt into sulphate of soda as a preliminary step in the manufacture of carbonate of soda. To save the expense of transporting the acid for this purpose, the *vitriol chambers* form part of the plant of the alkali works.

To convert this weak acid into the ordinary oil of vitriol of commerce, it is run off into shallow leaden pans set in brickwork, and supported on iron bars over the flue of a furnace, where it is heated until so much water has evaporated that the specific gravity of the acid has increased to 1·72. The concentration cannot be carried further in leaden pans, because the strong acid acts upon the lead, and converts it into sulphate—



$$2(H_2O.SO_3) + Pb = PbO.SO_3 + 2H_2O + SO_2.$$

The acid of 1·72 sp. gr. contains about 80 per cent. of true oil of vitriol ($H_2O.SO_3$), and is largely employed for making superphosphate of lime, and in other rough chemical manufactures. It is technically called *brown acid*, having acquired a brown colour from organic matter accidentally present in it.

To convert this brown acid into commercial oil of vitriol, it is boiled down, either in glass retorts or platinum stills, when water distils over, accompanied by a little sulphuric acid, and the acid in the retort becomes colourless, the brown carbonaceous matter being oxidised by the strong sulphuric acid, with formation of carbonic and sulphurous acids. When dense white fumes of oil of vitriol begin to pass over, showing that all the superfluous water has been expelled, the acid is drawn off by a siphon.

The very diluted acid which distils off is employed instead of water on the floor of the leaden chamber.

The cost of the acid is very much increased by this concentration. It cannot be conducted in open vessels, partly on account of the loss of sulphuric acid, partly because concentrated sulphuric acid absorbs moisture from the open air even at the boiling point. The loss by breakage of the glass retorts is very considerable, although it is reduced as far as possible by heating them in sand, and keeping them always at about the same temperature by supplying them with hot acid. But the boiling point of the concentrated acid is very high (640° F.), and the retorts consequently become so hot that a current of cold air or an accidental splash of acid will frequently crack them at once. Moreover the acid boils with *succussion* or violent bumping, caused by sudden bursts of vapour, which endanger the safety of the retort.

With platinum stills the risk of fracture is avoided, and the distillation may be conducted more rapidly, the brown acid (sp. gr. 1·72) being admitted at the top, and the oil of vitriol (sp. gr. 1·84) drawn off by a platinum siphon from the bottom of the still, which is protected from the open fire by an iron jacket. But since a platinum still will cost £2000 or £3000, the interest upon its value increases the cost of production of the acid.

When the perfectly pure acid is required, it is actually distilled over so as to leave the solid impurities (sulphate of lead, &c.,) behind in the retort. Some fragments of rock crystal should be introduced into the retort to moderate the bursts of vapour, and heat applied by a ring gas-burner with somewhat divergent jets.

Divested of working details, this most important chemical manufacture may be thus described:—

A mixture of sulphurous acid, air, steam, and a little vapour of nitric acid, is introduced into a leaden chamber containing a layer of water. The nitric acid is reduced by the sulphurous acid to the state of nitric oxide (NO), which takes up oxygen from the air (forming NO_2), and gives it to the sulphurous acid, which it converts into sulphuric acid. This is absorbed by the water, forming diluted sulphuric acid, which is concentrated by evaporation, first in leaden pans, and afterwards in glass retorts or platinum stills.

Properties of oil of vitriol.—The properties of concentrated sulphuric acid are very characteristic. Its great weight (sp. gr. 1·842), freedom from odour, and oily appearance, distinguish it from any other liquid commonly met with, which is fortunate, because it is difficult to preserve a label upon the bottles of this powerfully corrosive acid. Although, if absolutely pure, it is perfectly colourless, the ordinary acid used in the laboratory has a peculiar grey colour, due to traces of organic matter. Its high boiling-point (640° F.) has been already noticed; and although its vapour is perfectly transparent in the vessel in which the acid is boiled, as soon as it issues into the air it condenses into voluminous dense clouds of a most irritating description. Even a drop of the acid evaporated in an open dish will fill a large space with these clouds. Oil of vitriol solidifies when cooled to about − 30° F., but the acid once solidified requires a much higher temperature to liquefy it again. Oil of vitriol rapidly corrodes the skin and other organic textures upon which it falls, usually charring or blackening them at the same time. Poured upon a piece of wood, the latter speedily assumes a dark brown colour; and if a few lumps of sugar be dissolved in a very little water, and stirred with oil of vitriol, a violent action takes place, and a semi-solid black mass is produced. This property of sulphuric acid is turned to account in the manufacture of blacking, in which treacle and oil of vitriol are employed. These effects are to be ascribed to the powerful attraction of oil of vitriol for water. Woody fibre ($C_6H_{10}O_5$) (which composes the bulk of wood, paper, and linen), and sugar, ($C_{12}H_{22}O_{11}$), may be regarded, for the purpose of this explanation, as composed of carbon associated with 5 and 11

molecules of water, and any cause tending to remove the water would tend to eliminate the carbon.

The great attraction of this acid for water is shown by the high temperature (often exceeding the boiling point of water) produced on mixing oil of vitriol with water, which renders it necessary to be careful in diluting the acid.

The water should be placed in a jug, and the oil of vitriol poured into it in a thin stream, a glass rod being used to mix the acid with the water as it flows in. Ordinary oil of vitriol becomes turbid when mixed with water, from the separation of sulphate of lead (formed from the evaporating pans), which is soluble in the concentrated but not in the diluted acid, so that if the latter be allowed to stand for a few hours, the sulphate of lead settles to the bottom, and the clear acid may be poured off free from lead. Diluted sulphuric acid has a smaller bulk than is occupied by the acid and water before mixing.

Even when largely diluted, sulphuric acid corrodes textile fabrics very rapidly, and though the acid be too dilute to appear to injure them at first, it will be found that the water evaporates by degrees, leaving the acid in a more concentrated state, and the fibre is then perfectly rotten. The same result ensues at once on the application of heat; thus, if characters be written on paper with the diluted acid, they will remain invisible until the paper is held to the fire, when the acid will char the paper, and the writing will appear intensely black.

If oil of vitriol be left exposed to the air in an open vessel, it very soon increases largely in bulk from the absorption of water, and a flat dish of oil of vitriol under a glass shade (fig. 212) is frequently employed in the laboratory for drying substances without the assistance of heat. The drying is of course much accelerated by placing the dish on the plate of an air-pump, and exhausting the air from the shade, so as to effect the drying *in vacuo*. It will be remembered also that oil of vitriol is in constant use for drying gases.

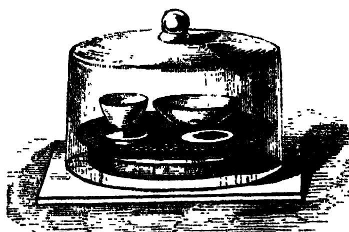
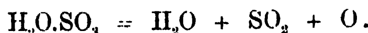


Fig. 212.—Drying over oil of vitriol.

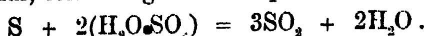
At a red heat, the vapour of oil of vitriol is decomposed into water, sulphurous acid, and oxygen—



$$H_2O.SO_3 = H_2O + SO_2 + O.$$

This decomposition takes place most easily when the vapour is passed through a strongly heated tube of platinum, and it has been taken advantage of for the preparation of oxygen, the sulphurous acid being absorbed by passing the mixed gases through lime. Reflecting upon the manufacture of oil of vitriol, it will be perceived that the oxygen thus obtained was originally derived from the air.

When sulphur is boiled with oil of vitriol, the latter gradually dissolves the melted sulphur, converting it into sulphurous acid—



$$S + 2(H_2O.SO_3) = 3SO_2 + 2H_2O.$$

All ordinary metals are acted upon by concentrated sulphuric acid when heated, except gold and platinum (this last even does not quite escape when long boiled with the acid), the metal being oxidised by one portion of the acid, which is thus converted into sulphurous acid, the oxide combining with another part of the sulphuric acid to form a sulphate. Thus,

when silver is boiled with strong sulphuric acid, it is converted into sulphate of silver, which is soluble in hot water—



$$Ag_2 + 2(H_2O.SO_3) = Ag_2O.SO_3 + 2H_2O + SO_2.$$

Should the silver contain any gold, it is left behind in the form of a dark powder. Sulphuric acid is extensively employed for the separation or *parting* of silver and gold. This acid is also employed for extracting gold from copper; and when sulphate of copper is manufactured by dissolving that metal in sulphuric acid (see p. 199), large quantities of gold are sometimes extracted from the accumulated residue left undissolved by the acid. If the sulphuric acid contains nitric acid, it dissolves a considerable quantity of gold, which separates again in the form of a purple powder when the acid is diluted with water, the sulphate of gold formed being reduced by the nitrous acid when the solution is diluted.

Some of the uses of sulphuric acid depend upon its specific action on certain organic substances, the nature of which has not yet been clearly explained. Of this kind is the conversion of paper into *vegetable parchment* by immersion in a cool mixture of two measures of oil of vitriol and one measure of water, and subsequent washing. The conversion is not attended by any change in the weight of the paper.

Beside oil of vitriol, sulphuric acid forms other definite combinations with water. By evaporating diluted sulphuric acid *in vacuo* at 212° F., an acid is left which has the composition $H_2O.SO_3.2H_2O$ (sp. gr. 1·63). If this acid be evaporated in air at 400° F., as long as steam escapes, the remaining acid has the composition $H_2O.SO_3.H_2O$ (sp. gr. 1·78). This acid is called *glacial sulphuric acid*, because it solidifies to a mass of ice-like crystals at 47° F.

145. *Anhydrous sulphuric acid* or *sulphuric anhydride*.—The mode of preparing this substance from the fuming sulphuric acid has already been noticed. It is more commonly obtained by expelling the water from bisulphate of soda ($Na_2O.H_2O.2SO_3$) by fusing it at a dull red heat, and afterwards distilling the anhydrous bisulphate ($Na_2O.2SO_3$) in an earthen retort, when neutral sulphate of soda ($Na_2O.SO_3$) is left, and the anhydrous sulphuric acid passing off as vapour may be condensed in a receiver cooled by ice.

Anhydrous sulphuric acid forms a white mass of crystals resembling asbestos; it fumes when exposed to air, since it emits vapour which condenses the moisture of the air, and it soon deliquesces from absorption of water, becoming hydrated sulphuric acid. When thrown into water it hisses like red-hot iron, from the sudden formation of steam. It fuses at 65° F., and boils at 110° F. The vapour is decomposed, as mentioned above, into sulphurous acid and oxygen, when passed through a red-hot tube. Phosphorus burns in its vapour, combining with the oxygen and liberating sulphur. Baryta glows when heated in the vapour of anhydrous sulphuric acid, and combines with it to form sulphate of baryta.

Anhydrous sulphuric acid is capable of combining with olefiant gas (C_2H_4) and oil-gas (C_4H_8), and absorbs these from mixtures of gases. In the analysis of coal-gas, a fragment of coke wetted with Nordhausen sulphuric acid is passed up into a measured volume of the gas standing over mercury, to absorb these illuminating hydrocarbons.

An interesting method of obtaining the anhydrous sulphuric acid consists in pouring 2 parts by weight of oil of vitriol over 3 parts of anhydrous

phosphoric acid, contained in a retort cooled in ice and salt, and afterwards distilling at a gentle heat, when the phosphoric acid retains the water, and the anhydrous sulphuric acid may be condensed in a cooled receiver.

Determination of the composition of sulphuric acid and oil of vitriol.—When 32 grains (one atomic weight) of sulphur are oxidised by boiling with nitric acid, the excess of nitric acid expelled by a moderate heat, the remaining hydrated sulphuric acid mixed with an *excess* of pure oxide of lead of known weight, say 300 grains, and all the water expelled by a high temperature, the mixture of sulphate and oxide of lead which is left is found to weigh 380 grains, showing that 32 parts of sulphur have combined with oxygen from the nitric acid to form 80 grains of sulphuric acid. Hence the sulphuric acid contains 32 grains of sulphur and 48 grains of oxygen, corresponding to the formula SO_3.

The vapour of SO_3 is found to be 43 times as heavy as hydrogen, which would give 86 for its molecular weight (p. 36). By treating a known weight of oil of vitriol with an excess of oxide of lead, and expelling the water by heat, it is found that 80 grains of SO_3 are combined with 18 grains of water. Hence oil of vitriol contains $H_2O.SO_3$. Its vapour, therefore, should be 49 times as heavy as hydrogen; but experiment shows it to be only 24 times as heavy (at 880° F.); this appears to be due to the temporary decomposition (or *dissociation*) of the two volumes of oil of vitriol into two volumes of water and two volumes of sulphuric acid. This deprives us of the usual evidence as to the molecular weight of a compound.

On examining the behaviour of oil of vitriol with caustic potash or soda, it is found that two salts of each alkali may be obtained, a sulphate and a bisulphate; thus the sulphate of potash is $K_2O.SO_3$, or K_2SO_4, and the bisulphate is $K_2O.H_2O, 2SO_3$ or $KHO.SO_3$, or $KHSO_4$, showing that the hydrogen can be replaced by halves, and that therefore at least two atoms of hydrogen must be contained in the molecule of oil of vitriol. The presence of these two atoms of hydrogen replaceable by a metal is implied by saying that the oil of vitriol is a *dibasic* or *bibasic* acid.

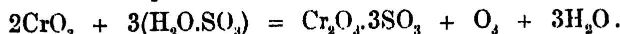
146. *Sulphates. Action of sulphuric acid upon metallic oxides.*—At common temperatures sulphuric acid has a more powerful attraction for bases than any other acid, and is therefore capable of displacing all other acids from their salts; many cases will be remembered in which this power of sulphuric acid is turned to account.

So great is the acid energy of sulphuric acid, that when it is allowed to act upon an indifferent or acid metallic oxide, it causes the separation of a part of the oxygen, and combines with the basic oxide so produced. Advantage is sometimes taken of this circumstance for the preparation of oxygen; for instance, when binoxide of manganese is heated with sulphuric acid, sulphate of manganese is produced, and oxygen disengaged.



$$MnO_2 + H_2O.SO_3 = MnO.SO_3 + O + H_2O.$$

Again, if chromic acid be treated in the same way, sulphate of sesquioxide of chromium will be produced, with liberation of oxygen—



$$2CrO_3 + 3(H_2O.SO_3) = Cr_2O_3.3SO_3 + O_3 + 3H_2O.$$

A mixture of bichromate of potash ($K_2O.2CrO_3$) and sulphuric acid is sometimes used as a source of oxygen.

Many bases are capable of forming two salts with sulphuric acid, a neutral sulphate and an acid sulphate. The acid sulphates may be represented as compounds of the neutral sulphates with hydrated sulphuric acid; thus, the neutral sulphate of potash is $K_2O.SO_3$, and the bisulphate is $K_2O.SO_3, H_2O.SO_3$. The latter, being a solid salt which possesses, at high temperatures, almost all the acid energy of sulphuric acid, is most useful in blowpipe and metallurgic experiments. When strongly heated, this salt parts with hydrated sulphuric acid, and neutral sulphate of potash is left. It has been seen that bisulphate of soda ($Na_2O.SO_3, H_2O.SO_3$)

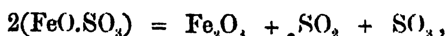
parts with its water when heated, and becomes $Na_2O.2SO_3$. Crystals of anhydrous bisulphate of potash $K_2O.2SO_3$ have also been obtained.

Sulphuric acid forms a large number of double salts in which two sulphates are combined together. The large class of *alums* yields examples of these, in which one of the sulphates contains an alkaline base, and the other a basic sesquioxide. *Potash-alum*, for example, is represented by the formula $K_2O.SO_3,Al_2O_3.3SO_3.24Aq$, being a double sulphate of alumina and potash.

The following table exhibits the composition of the sulphates most frequently met with :—

Chemical Name.	Common Name.	Additive Formula.	Substitutive Formula.
Sulphate of potash	Sal polychrest	$K_2O.SO_3$	K_2SO_4
Sulphate of soda	Glauber's Salt	$Na_2O.SO_3.10H_2O$	$Na_2SO_4.10H_2O$
Bisulphate of potash		$K_2O.SO_3,\ H_2O.SO_3$	$KHSO_4$
Sulphate of ammonia		$2NH_3.H_2O\ SO_3$	$(NH_4)_2SO_4$
Sulphate of baryta	Heavy spar	$BaO\ SO_3$	$BaSO_4$
Sulphate of lime	Gypsum	$CaO.SO_3.2H_2O$	$CaSO_4.2H_2O$
Sulphate of magnesia	Epsom salts	$MgO.SO_3.7H_2O$	$MgSO_4.7H_2O$
Double sulphate of alumina and potash	Potash-alum	$K_2O.SO_3,\ Al_2O_3.3SO_3.24H_2O$	$KAl2SO_4.12H_2O$
Double sulphate of alumina and ammonia	Ammonia-alum	$2NH_3.H_2O.SO_3,\ Al_2O_3.3SO_3.24H_2O$	$NH_4Al\,2SO_4.12H_2O$
Double sulphate of chromium and potash	Chrome-alum	$K_2O.SO_3,\ Cr_2O_3.3SO_3.24H_2O$	$KCr\,2SO_4.12H_2O$
Sulphate of iron	Green vitriol Copperas	$FeO.SO_3.7H_2O$	$FeSO_4.7H_2O$
Sulphate of manganese		$MnO.SO_3.5H_2O$	$MnSO_4.5H_2O$
Sulphate of zinc	White vitriol	$ZnO.SO_3.7H_2O$	$ZnSO_4.7H_2O$
Sulphate of lead		$PbO.SO_3$	$PbSO_4$
Sulphate of copper	Blue vitriol Blue stone	$CuO.SO_3.5H_2O$	$CuSO_4.5H_2O$

In consequence of the tendency of sulphuric acid to break up into sulphurous acid and oxygen at a high temperature, most of the sulphates are decomposed by heat; sulphate of copper, for example, when very strongly heated, leaves oxide of copper, whilst sulphurous acid and oxygen escape; $CuO.SO_3 = CuO + SO_2 + O$. Sulphate of iron is more easily decomposed, because of the attraction of the protoxide of iron for the oxygen, with which it combines to form sesquioxide—



$$2(FeO.SO_3) = Fe_2O_3 + SO_2 + SO_3,$$

part of the acid escaping in the anhydrous state.

Sulphate of zinc ($ZnO.SO_3$) has been proposed as a source of oxygen upon the large scale, since it is a very cheap salt, and when strongly heated, yields a residue of oxide of zinc which is useful as a white paint, whilst sulphurous acid and oxygen gases escape, the former of which may

be absorbed by lime or soda, yielding sulphites which are useful in the arts.

The neutral sulphates of potash, soda, baryta, strontia, lime, and oxide of lead are not decomposed by heat, and sulphate of magnesia is only partly decomposed at a very high temperature.

When a sulphate is heated with charcoal, the carbon removes the whole of the oxygen, and a sulphide of the metal remains, thus—



$$K_2O.SO_3 \text{ (Sulphate of potash)} + C_4 = K_2S \text{ (Sulphide of potassium)} + 4CO.$$

Hydrogen, at a high temperature, effects a similar decomposition.

Even at the ordinary temperature, sulphate of lime in solution is sometimes deoxidised by organic matter; this may occasionally be noticed in well and river waters when kept in closed vessels; they acquire a strong smell of hydrosulphuric acid, in consequence of the conversion of a part of the sulphate of lime into sulphide of calcium by the organic constituents of the water, and the subsequent decomposition of the sulphide of calcium by the carbonic acid present in the water.

147. *Hyposulphurous acid.**—This acid has not been obtained either in the anhydrous state or in combination with water; but as many salts are known which contain, in addition to a metallic oxide, sulphur and oxygen in the proportions expressed by the formula S_2O_2, many chemists assume the existence of hyposulphurous acid, having that composition, in such salts, which are therefore called *hyposulphites.*

The *hyposulphite of soda* is by far the most important of these salts, being very largely employed in photography, and as a substitute for sulphite of soda as an *antichlore.* The simplest method of preparing it consists in digesting powdered roll sulphur with solution of sulphite of soda ($Na_2O.SO_2$), when the latter dissolves an atom of sulphur and becomes hyposulphite of soda ($Na_2O.S_2O_2$ or $Na_2S_2O_3$), which crystallises from the solution, when sufficiently evaporated, in fine prismatic crystals, having the formula $Na_2S_2O_3.5H_2O$.

On a large scale, the hyposulphite of soda is more economically prepared from the hyposulphite of lime obtained by exposing the refuse (*tank-waste* or *soda-waste*) of the alkali-works to the air for some days. This refuse contains a large proportion of sulphide of calcium, which becomes converted into hyposulphite of lime by oxidation—



$$2CaS + O_4 = CaS_2O_3 + CaO.$$

The hyposulphite of lime is dissolved out by water, and the solution mixed with carbonate of soda, when carbonate of lime is precipitated and hyposulphite of soda remains in solution—



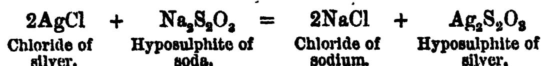
$$CaS_2O_3 + Na_2O.CO_2 = CaO.CO_2 + Na_2S_2O_3.$$

The most remarkable and useful property of the hyposulphite of soda is that of dissolving the chloride and iodide of silver, which are insoluble in water and most other liquids.

On mixing a solution of nitrate of silver with one of chloride of sodium, a white precipitate of chloride of silver is obtained, the separation of which is much promoted by stirring the liquid; $AgNO_3 + NaCl = AgCl + NaNO_3$. The precipitate may be allowed to settle and washed twice or thrice by decantation. One portion of the chloride of silver is transferred to another glass, mixed with water, and solution of hyposulphite of soda added by degrees. The chloride of silver is very easily dissolved, yielding an intensely sweet solution, which contains the hyposulphite of

* Ὑπό, *under*, containing less oxygen than sulphurous acid.

silver, produced by double decomposition between the chloride of silver and hypo sulphite of soda—



$$2AgCl + Na_2S_2O_3 = 2NaCl + Ag_2S_2O_3$$

Chloride of silver. Hyposulphite of soda. Chloride of sodium. Hyposulphite of silver.

The hyposulphite of silver combines with the excess of hyposulphite of soda to form the double salt $Ag_2S_2O_3.2(Na_2S_2O_3)$, which may be obtained in extremely sweet crystals from the solution.

If the other portion of the chloride of silver be exposed to the action of light, and especially of direct sunlight, it assumes by degrees a dark slate colour, from the formation of subchloride of silver, chlorine being set free; $2AgCl = Ag_2Cl + Cl$. By treating this darkened chloride of silver with hyposulphite of soda, as before, the unaltered chloride of silver will be entirely dissolved, but the subchloride will be decomposed into chloride of silver, which dissolves in the hyposulphite, and metallic silver, which is left in a very finely divided state as a black powder; $Ag_2Cl = AgCl + Ag$. The application of these facts in photography is well illustrated by the following experiments. A sheet of paper is soaked for a minute or two in a solution of 10 grains of common salt in an ounce of water contained in a flat dish. It is then dried, and soaked for three minutes in a solution of 50 grains of nitrate of silver in an ounce of water. The paper thus becomes impregnated with chloride of silver formed by the decomposition between the chloride of sodium and the nitrate of silver. It is now hung up in a dark place to dry. If a piece of lace, or a fern leaf, or an engraving on thin paper, with well marked contrast of light and shade, be laid upon a sheet of the prepared paper, pressed down upon it by a plate of glass, and exposed for a short time to sunlight, a perfect representation of the object will be obtained, those parts of the sensitive paper to which the light had access having been darkened by the formation of subchloride of silver, whilst those parts which were protected from the light remain unchanged.

But if this photographic print were again exposed to the action of light, it would soon be obliterated, the unaltered chloride of silver in the white parts being acted on by light in its turn. The print is therefore *fixed* by soaking it for a short time in a saturated solution of hyposulphite of soda, which dissolves the white unaltered chloride of silver entirely, and decomposes the subchloride formed by the action of light, leaving the black finely-divided metallic silver in the paper. The print should now be washed for two or three hours in a gentle stream of water, to remove all the hyposulphite of silver, when it will be quite permanent.

The power of hyposulphite of soda to dissolve chloride of silver has also been turned to account for extracting that metal from its ores, in which it is occasionally present in the form of chloride.

The behaviour of solution of hyposulphite of soda with powerful acids explains the circumstance that the hyposulphurous acid has not been isolated, for if the solution be mixed with a little diluted sulphuric or hydrochloric acid, it remains clear for a few seconds, and then becomes suddenly turbid from the separation of sulphur, at the same time evolving a powerful odour of sulphurous acid; $S_2O_2 = S + SO_2$. This disposition of the hyposulphurous acid to break up into sulphurous acid and sulphur also explains the precipitation of metallic sulphides, which often takes place when hyposulphite of soda is added to the acid solutions of the metals. Thus if an acid solution of chloride of antimony (obtained by boiling crude antimony ore (Sb_2S_3) with hydrochloric acid) be added to a boiling solution of hyposulphite of soda, the sulphur separated from the hyposulphurous acid combines with the antimony to form a fine orange-red precipitate of sulphide of antimony (Sb_2S_3), which is used in painting under the name of *antimony vermilion.* On the large scale the solution of hyposulphite of lime obtained from the alkali waste is employed in the preparation of antimony vermilion, as being less expensive than the soda-salt.

Instead of adding sulphur to sulphurous acid, hyposulphurous acid in

combination may be obtained by removing oxygen from the former acid. Thus if an aqueous solution of sulphurous acid be acted on by zinc, one portion of the acid is deoxidised and converted into hyposulphurous acid, which combines with the oxide of zinc—



$$3SO_2 + Zn_2 = ZnO.SO_2 + ZnS_2O_3 .$$

The presence of hyposulphite in the solution may be proved by adding hydrochloric acid.

When crystals of hyposulphite of soda are heated in the air, they first fuse in their water of crystallisation, then dry up to a white mass, which burns with a blue flame, leaving a residue of sulphate of soda. If heated out of contact with air, pentasulphide of sodium will be left with the sulphate of soda—



$$4(Na_2S_2O_35H_2O) = 20H_2O + 3(Na_2O.SO_3) + Na_2S_5 .$$

Some of the reactions of hyposulphite of soda become more intelligible when the salt is represented as sulphate of soda (Na_2SO_4) in which an atom of sulphur has displaced an atom of oxygen (Na_2SO_3S).

148. *Hyposulphuric acid* or *dithionic acid* ($H_2S_2O_6$) has not at present acquired any practical importance, and has not been obtained in the anhydrous state. To prepare a solution of the acid, binoxide of manganese in a state of fine division is suspended in water and exposed to a current of sulphurous acid gas, the water being kept very cold whilst the gas is passing. A solution of hyposulphate of manganese is thus obtained; $2SO_2 + MnO_2 = MnS_2O_6$. Some sulphate of manganese is always formed at the same time; $SO_2 + MnO_2 = MnO.SO_3$, and if the temperature be allowed to rise, this will be produced in large quantity.

The solution containing sulphate and hyposulphate of manganese is decomposed by solution of baryta (baryta-water), when the oxide of manganese is precipitated, together with sulphate of baryta, and hyposulphate of baryta is left in solution. To the filtered solution diluted sulphuric acid is carefully added until all the baryta is precipitated as sulphate of baryta, when the solution of hyposulphuric acid is filtered off and evaporated *in vacuo* over oil of vitriol. It forms a colourless inodorous liquid, which is decomposed when heated, into hydrated sulphuric and sulphurous acids; $H_2S_2O_6 = H_2O.SO_3 + SO_2$. Oxidising agents (nitric acid, chlorine, &c.) convert it into sulphuric acid.

The *hyposulphates* are not of any practical importance; they are all soluble, and are decomposed by heat, leaving sulphates, and evolving sulphurous acid.

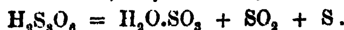
149. *Trithionic acid* ($H_2S_3O_6$), or *sulphuretted hyposulphuric acid*, is also a practically unimportant acid, not known in the anhydrous state. Its hydrate is prepared from the trithionate of potash, which is formed by boiling a strong solution of bisulphite of potash with sulphur until the solution becomes colourless, and filtering the hot solution from any undissolved sulphur—



$$3(K_2O.H_2O.2SO_2) + S = 2(K_2S_3O_6) + K_2O.SO_2 + 3H_2O .$$

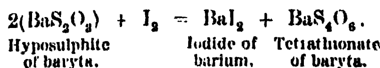
Bisulphite of potash. Trithionate of potash.

The solution deposits trithionate of potash in prismatic crystals. By dissolving these in water, and decomposing the solution with perchloric acid, the potash is precipitated as perchlorate, and a solution of trithionic acid is produced, from which the hydrated acid has been obtained in crystals. It is, however, very unstable, being easily resolved into sulphurous acid, sulphuric acid, and free sulphur—



$$H_2S_3O_6 = H_2O.SO_3 + SO_2 + S .$$

150. *Tetrathionic acid*, or *bisulphuretted hyposulphuric acid* ($H_2S_4O_6$) is rather more stable than the preceding acid, though equally devoid of practical importance. It is formed when hyposulphite of baryta, suspended in a little water, is treated with iodine, when tetrathionate of baryta is obtained in crystals—

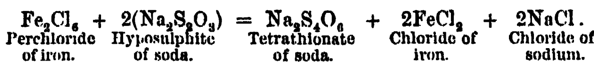


$$2(BaS_2O_3) + I_2 = BaI_2 + BaS_4O_6 .$$

Hyposulphite of baryta. Iodide of barium. Tetrathionate of baryta.

By exactly precipitating the baryta from a solution of the tetrathionate by addition of diluted sulphuric acid, the solution of tetrathionic acid may be obtained. When the solution is boiled, it is decomposed into sulphuric and sulphurous acids and free sulphur ; $H_2S_4O_6 = H_2O.SO_3 + SO_2 + S_2$.

When solution of perchloride of iron is added to hyposulphite of soda, a fine purple colour is at first produced, which speedily vanishes, leaving a colourless solution. The purple colour appears to be due to the formation of the hyposulphite of sesquioxide of iron, which speedily decomposes, the ultimate result being expressed by the equation—



$$\underset{\text{Perchloride of iron.}}{Fe_2Cl_6} + \underset{\text{Hyposulphite of soda.}}{2(Na_2S_2O_3)} = \underset{\text{Tetrathionate of soda.}}{Na_2S_4O_6} + \underset{\text{Chloride of iron.}}{2FeCl_2} + \underset{\text{Chloride of sodium.}}{2NaCl}.$$

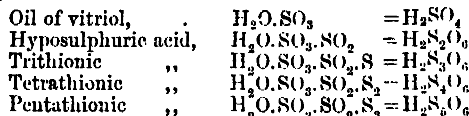
151. *Pentathionic acid* ($H_2S_5O_6$) possesses some interest as resulting from the action of sulphuretted hydrogen upon sulphurous acid, when much sulphur is deposited, and pentathionic acid remains in solution—



$$5H_2S + 5SO_2 = \underset{\text{Pentathionic acid.}}{H_2S_5O_6} + 4H_2O + S_5.$$

To obtain a concentrated solution of the acid, sulphuretted hydrogen and sulphurous acid are passed alternately through the same portion of water until a large deposition of sulphur has taken place. This is allowed some hours to settle ; the clear liquid poured off and the solution concentrated by evaporation, first over a water-bath, and, finally, *in vacuo*, over oil of vitriol, for a concentrated solution of pentathionic acid is decomposed by heat into sulphuric and sulphurous acids, with separation of sulphur ; $H_2S_5O_6 = H_2O.SO_3 + SO_2 + S_3$.

The true constitution of the preceding (*polythionic*) acids is not yet understood, but it may assist the memory to retain the usual mode of decomposition of the acids if they are represented as derived from oil of vitriol by successive additions of sulphurous acid and sulphur, thus—



Oil of vitriol, .	$H_2O.SO_3$	$=H_2SO_4$
Hyposulphuric acid,	$H_2O.SO_3.SO_2$	$=H_2S_2O_6$
Trithionic ,,	$H_2O.SO_3.SO_2.S$	$=H_2S_3O_6$
Tetrathionic ,,	$H_2O.SO_3.SO_2.S_2$	$=H_2S_4O_6$
Pentathionic ,,	$H_2O.SO_3.SO_2.S_3$	$=H_2S_5O_6$

Bisulphide of Carbon.

$CS_2 = 76$ parts by weight.

152. This very important compound (also called *bisulphuret of carbon*) is found in small quantity among the products of destructive distillation of coal, and is very largely manufactured for use as a solvent for sulphur, phosphorus, caoutchouc, fatty matters, &c. It is one of the few compounds of carbon which can be obtained by the direct union of their elements, and is prepared by passing vapour of sulphur over charcoal heated to redness.

In small quantity, bisulphide of carbon is easily prepared in a tube of German glass (combustion-tube) about two feet long and half-an-inch in diameter (fig. 213).

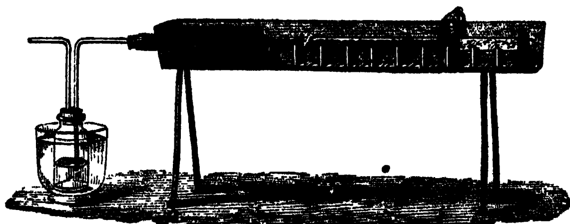


Fig. 213.

This tube is closed at one end, and a few fragments of sulphur dropped into it, so as to occupy two or three inches. The rest of the tube is filled up with small frag-

ments of recently calcined wood charcoal. The tube is placed in a combustion-furnace, and its open end connected by a perforated cork with a glass tube, which dips just below the surface of water contained in a bottle placed in a vessel of very cold water. That part of the tube which contains the charcoal is first surrounded with red-hot charcoal, and when it is heated to redness, a little red-hot charcoal is placed near the end containing the sulphur (hitherto protected by a sheet-iron screen), so that the vapour of sulphur may be slowly passed over the red-hot charcoal. The bisulphide of carbon being insoluble in water, and much heavier (sp. gr. 1·27), is deposited beneath the water in the receiver. To purify the bisulphide of carbon from the water and the excess of sulphur which is deposited with it, the water is carefully drawn off with a small siphon, the bisulphide of carbon transferred to a flask, and a few fragments of chloride of calcium dropped into it to absorb the water. A bent tube connected with a Liebig's condenser, or with a worm, is attached to the flask (fig. 214) by a perforated cork, and the flask is gently heated in a water bath, when the bisulphide of carbon is distilled over as a perfectly colourless liquid. The inflammability of the bisulphide of carbon renders great care necessary.

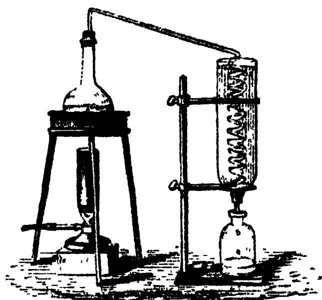


Fig. 214.

On a large scale, a fire-clay retort is filled with fragments of charcoal and heated to redness, pieces of sulphur being occasionally dropped in through an earthenware tube passing to the bottom of the retort. When very large quantities are made, coke is employed, and the vapour of sulphur is obtained from iron pyrites. The bisulphide of carbon is possessed of some very remarkable properties: it is a very brilliant liquid, the light passing through which is partly decomposed into its component coloured rays before it reaches the eye. These properties are dependent upon its high refractive and dispersive powers, which are turned to great advantage in optical experiments, especially in *spectrum analysis*, where the rays emanating from a coloured flame are analysed by passing them through a prismatic bottle filled with bisulphide of carbon. It is also highly *diathermanous*, that is, it allows rays of heat to pass through it with comparatively little loss, so that if it be rendered opaque to light by dissolving iodine in it, the rays of light emanating from a luminous object may be arrested, whilst the calorific rays are allowed to pass. It has never been frozen, and is therefore employed in thermometers for measuring very low temperatures. Bisulphide of carbon is a very volatile liquid, readily assuming the form of vapour at the ordinary temperature, and boiling at 118°·5 F. Its vapour, when diluted with air, has a very disgusting and exaggerated odour of sulphuretted hydrogen, but the smell at the mouth of the bottle is ethereal and not unpleasant.

The rapid evaporation of bisulphide of carbon is, of course, productive of great cold. If a few drops be placed in a watch-glass and blown upon, they soon pass off in vapour, and the temperature of the glass is so reduced that the moisture of the breath condenses upon it in hoar-frost, which melts when the glass is placed in the palm of the hand. If a glass plate be covered with water, a watch-glass containing bisulphide of carbon placed on it, and evaporation promoted by blowing through a tube, the watch-glass will be frozen on to the plate, so that the latter may be lifted up by it.

The bisulphide of carbon is exceedingly inflammable; it takes fire at a temperature far below that required to inflame ordinary combustible bodies, and burns with a bright blue flame, producing carbonic and sul-

phurous acids ($CS_2 + O_6 = CO_2 + 2SO_2$), and having a great tendency to deposit sulphur unless the supply of air is very good.

If a little bisulphide of carbon be dropped into a small beaker, it may be inflamed by holding in its vapour a test-tube containing oil heated to about 300° F., which will be found incapable of firing gunpowder or of inflaming any ordinary combustible substance.

The abundance of sulphur separated in the flame of bisulphide of carbon enables it to burn iron by converting it into sulphide. If some bisulphide of carbon be boiled in a test-tube provided with a piece of glass tube from which the vapour may be burnt, and a piece of thin iron wire be held in the flame (fig. 215), it will burn with vivid scintillation, the fusible sulphide of iron dropping off.

The vapour of bisulphide of carbon acts very injuriously if breathed for any length of time, producing symptoms somewhat resembling those caused by sulphuretted hydrogen. Its poisonous properties have been turned to account for killing insects in grain without injuring it.

The chief applications of bisulphide of carbon depend upon its power of dissolving the oils and fats. After as much oil as possible has been extracted from seeds and fruits by pressure, a fresh quantity is obtained by treating the pressed cake with bisulphide of carbon, which is afterwards recovered by distillation from the oil. In Algiers, bisulphide of carbon is employed for extracting the essential oils in which reside the perfumes of roses, jasmine, lavender, &c.

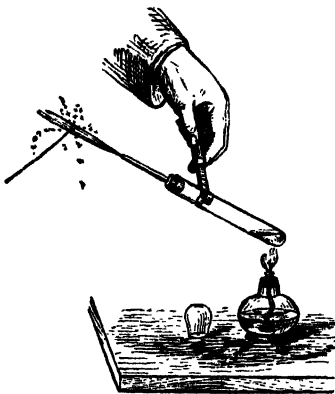
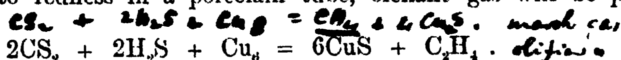


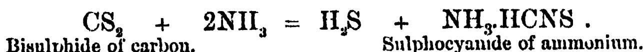
Fig. 215.

Bisulphide of carbon has often been made a starting point in the attempts to produce organic compounds by synthesis. It may be employed in the formation of the hydrocarbons which are usually derived from organic sources, for if it be mixed with sulphuretted hydrogen (by passing that gas through a bottle containing bisulphide of carbon gently warmed), and passed over copper-turnings heated to redness in a porcelain tube, olefiant gas will be produced—



$$2CS_2 + 2H_2S + Cu_8 = 6CuS + C_2H_4 .$$

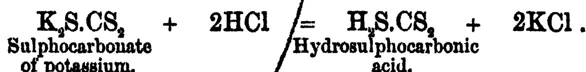
The action of bisulphide of carbon upon ammonia is practically important for the easy production of *sulphocyanide of ammonium*, which is formed when the bisulphide of carbon is dissolved in alcohol, and acted on by ammonia with the aid of heat—



$$\underset{\text{Bisulphide of carbon.}}{CS_2} + 2NH_3 = H_2S + \underset{\text{Sulphocyanide of ammonium.}}{NH_3.HCNS} .$$

Bisulphide of carbon is the sulphur-acid corresponding to carbonic acid, and is often called sulphocarbonic acid; it combines with some of the sulphur-bases to form *sulphocarbonates*, which correspond to the carbonates, containing sulphur in place of oxygen. Thus, when a solution of sulphide of potassium is mixed with an excess of bisulphide of carbon, the sulphocarbonate of (sulphide of) potassium is obtained in orange-yellow crystals. Even the hydrogen compound corresponding in composition to the unknown hydrate of carbonic acid may be obtained as a

yellow oily liquid by decomposing sulphocarbonate of potassium with hydrochloric acid—



$$K_2S.CS_2 + 2HCl = H_2S.CS_2 + 2KCl.$$

Sulphocarbonate of potassium. Hydrosulphocarbonic acid.

As would be expected, the sulphocarbonates, when boiled with water, exchange their sulphur for oxygen, becoming carbonates—



$$K_2S.CS_2 + 3H_2O = K_2O.CO_2 + 3H_2S.$$

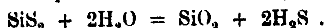
The bisulphide of carbon vapour in coal-gas is one of the most injurious of the impurities, and one of the most difficult to remove with economy. It is especially injurious, because when burning in the presence of aqueous vapour, a part of its sulphur is converted into sulphuric acid, the corrosive effects of which are so damaging. Several processes have been devised for its removal. The gas has been washed with the *ammoniacal liquor* (containing hydrosulphate of ammonia) which absorbs the bisulphide. Steam, at a high temperature, has been employed to convert it into hydrosulphuric and carbonic acids, which are both easily removed from the gas; $CS_2 + 2H_2O = CO_2 + 2H_2S$. Lime at a red heat decomposes it in a similar way; $CS_2 + 3CaO = CaO.CO_2 + 2CaS$. Oxide of lead dissolved in caustic soda has been used to convert it into sulphide of lead; $CS_2 + 2PbO + Na_2O = 2PbS + Na_2O.CO_2$. Its removal as sulphocarbonate by an alcoholic solution of potash or soda has also been proposed. At present, however, it retains its character as one of the most troublesome impurities with which the gas manufacturer has to deal.

Carbonic oxysulphide, COS = 60 parts by weight = 2 volumes. This compound, which may be regarded as hydrosulphuric acid in which CO has replaced H_2, is formed when a mixture of carbonic oxide with sulphur vapour is acted on by electric sparks, or passed through a red-hot porcelain tube.

It is easily prepared by gently heating the sulphocyanide of potassium with oil of vitriol diluted with four-fifths of its volume of water, and collecting the gas over mercury.

The action of the sulphuric acid upon the sulphocyanide produces hydrosulphocyanic acid; KCNS (sulphocyanide of potassium) + H_2SO_4 = HCNS + $KHSO_4$; which is then decomposed by the water, in the presence of the excess of sulphuric acid, into the carbonic oxysulphide gas and ammonia, which combines with the sulphuric acid; HCNS + H_2O = NH_3 + COS. The gas has a peculiar disagreeable odour, recalling that of bisulphide of carbon; it is more than twice as heavy as air (sp. gr. 2·11), and is very inflammable, burning with a blue flame, and yielding carbonic and sulphurous acid gases. Potash absorbs and decomposes it, yielding carbonate of potash and sulphide of potassium; $COS + 4KHO = K_2S + K_2O.CO_2 + 2H_2O$.

153. *Bisulphide of silicon* (SiS_2), corresponding in composition to bisulphide of carbon, is obtained by burning silicon in sulphur vapour, or by passing vapour of bisulphide of carbon over a mixture of silica and charcoal. Unlike the carbon compound, it is a white amorphous solid, absorbing moisture when exposed to air, and soluble in water, which gradually decomposes it into silicic and hydrosulphuric acids—



$$SiS_2 + 2H_2O = SiO_2 + 2H_2S.$$

When heated in air, it burns slowly, yielding silicic and sulphurous acids.

154. *Sulphide of nitrogen* (NS) is a yellow crystalline explosive substance, produced by a complicated reaction which takes place when chloride of sulphur, dissolved in bisulphide of carbon, is acted on by gaseous ammonia, when hydrochlorate of ammonia is deposited, and the filtered liquid, allowed to evaporate, deposits sulphide of nitrogen mixed with sulphur, which may be dissolved out by bisulphide of carbon, in which the nitrogen compound is nearly insoluble; this substance is remarkable for its sparing solubility, its irritating odour, and its explosibility when struck or moderately heated, its elements being held together by a very feeble attraction.

155. Chlorides of sulphur.—The *subchloride*, or *chloride of sulphur* (S_2Cl_2 = 135 parts by weight), is the most important of these, since it is employed in the process of vulcanising caoutchouc. It is very easily prepared by passing dry chlorine over sulphur very gently heated in a retort (fig. 216); the sulphur quickly melts, and the chloride of sulphur

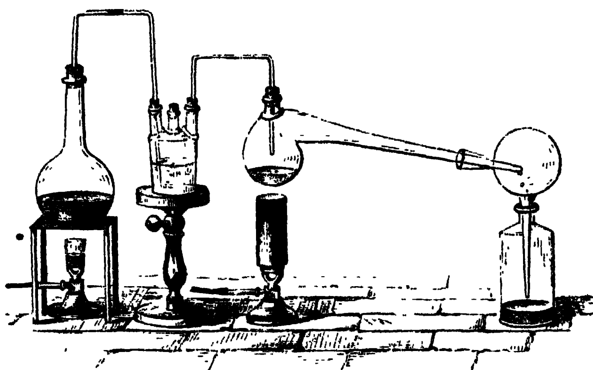


Fig. 216.—Preparation of chloride of sulphur.

distils over into the receiver as a yellow volatile liquid (boiling point, 280° F.), which has a most peculiar odour. It fumes strongly in air, the moisture decomposing it, forming hydrochloric and sulphurous acids, and causing a deposit of sulphur upon the neck of the bottle—



$$2S_2Cl_2 + 2H_2O = 4HCl + SO_2 + S_3 .$$

When poured into water, it sinks (sp. gr. 1·68) and slowly undergoes decomposition; the separated sulphur, of course, belongs to the electro-positive variety (see p. 191), and the solution contains, beside hydrochloric and sulphurous acids, some of the acids containing a larger proportion of sulphur. If phosphorus dissolved in bisulphide of carbon be mixed with chloride of sulphur, the liquid will take fire on addition of ammonia. The specific gravity of the vapour of chloride of sulphur is 4·7, showing that it is 68 times as heavy as hydrogen, giving for its molecular weight 136, which agrees very nearly with that calculated (135).

Bichloride of sulphur (SCl_2) is a far less stable compound than the chloride, from which it is obtained by the action of an excess of chlorine. It is a dark red fuming liquid, easily resolved, even by sunlight, into free chlorine and chloride of sulphur.

Iodide of sulphur (SI_2) is a crystalline unstable substance, produced by the direct union of its elements, and occasionally employed in medicine.

Subiodide of sulphur (S_2I_2) is obtained in large tabular crystals resembling iodine, by decomposing the subchloride of sulphur with iodide of ethyle; $S_2Cl_2 + 2C_2H_5I = S_2I_2 + 2C_2H_5Cl$.

Selenium.

Se = 79·5 parts by weight.

156. Selenium (Σελήνη, *the moon*) is a rare element, very closely allied to sulphur in its natural history, physical characters, and chemical relations to other bodies. It is found sparingly in the free state associated with some varieties of native sulphur, but more commonly in combination with metals, forming *selenides*, which are found together with the sulphides. The iron pyrites of Fahlun, in Sweden, is especially remarkable for the presence of selenium, and was the source whence this element was first obtained. The Fahlun pyrites is employed for the manufacture of

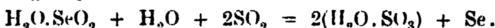
oil of vitriol, and in the leaden chambers a reddish brown deposit is found, which was analysed by Berzelius in 1817, and found to contain the new element.

In order to extract selenium from the seleniferous deposit of the vitriol works, it may be boiled with sulphuric acid diluted with an equal volume of water, and nitric acid added in small portions until the oxidation is completed, when no more red fumes will escape. The solution, containing selenious (SeO_2) and selenic (SeO_3) acids, is largely diluted with water, filtered off from the undissolved matters, mixed with about one-fourth of its bulk of hydrochloric acid, and somewhat concentrated by evaporation, when the hydrochloric acid reduces the selenic to selenious acid—



$$H_2O.SeO_3 + 2HCl = H_2O.SeO_2 + H_2O + Cl_2.$$

A current of sulphurous acid gas is now passed through the solution, when the selenium is precipitated in fine red flakes, which collect into a dense black mass when the liquid is gently heated—



$$H_2O.SeO_2 + H_2O + 2SO_2 = 2(H_2O.SO_3) + Se.$$

The proportion of selenium in the deposit from the leaden chambers is variable. The author has obtained above 3 per cent. by this process.

Selenium, like sulphur, is capable of existing in three allotropic states: the red amorphous variety precipitated from its solutions, or sublimed like flowers of sulphur; the black vitreous form; and the crystalline form deposited from its solution in bisulphide of carbon, in which it is far less easily dissolved than sulphur. When heated, it fuses easily, boils below a red heat, and is converted into a deep yellow vapour, which expands when heated in the same anomalous manner as vapour of sulphur.

Selenium is less combustible than sulphur; when heated in air it burns with a blue flame, and emits a peculiar odour like that of putrid horse-radish, which appears to be due to the formation of a little selenietted hydrogen from the moisture of the air. When heated with oil of vitriol, selenium forms a green solution which deposits the selenium again when poured into water.

Selenious acid (SeO_2), corresponding to sulphurous acid, is the product of combustion of selenium in oxygen. It is best obtained by dissolving selenium in boiling nitric acid (which would convert sulphur into sulphur*ic* acid), and evaporating to dryness, when the selenious acid remains as a white solid which sublimes in needle-like crystals when heated. When dissolved in boiling water, it yields a crystalline hydrate of selenious acid.

Selenic acid (SeO_3) is not known in the anhydrous state. It is formed when selenium is oxidised by fused nitre; $K_2O.N_2O_5 + Se = K_2O.SeO_3 + 2NO$. By dissolving the seleniate of potash in water, and adding nitrate of lead, a precipitate of seleniate of lead ($PbO.SeO_3$) is obtained, and if this be suspended in water and decomposed by passing hydrosulphuric acid gas, lead will be removed as insoluble sulphide, and a solution of hydrated selenic acid will be obtained—



$$PbO.SeO_3 + H_2S = H_2O.SeO_3 + PbS.$$

This solution may be evaporated till it has a sp. gr. of 2·6, when it very closely resembles oil of vitriol. It is decomposed, however, at about 550° F., evolving oxygen, and becoming selenious acid. It oxidises the metals like oil of vitriol, and even dissolves gold. The seleniates closely resemble the sulphates, but they are decomposed when heated with hydrochloric acid, chlorine being evolved, and selenious acid produced.

Hydroselenic acid, or *selenietted hydrogen* (H_2Se), is the exact parallel of sulphuretted hydrogen, and is produced by a similar process. It is even more offensive and poisonous than that gas, and acts in a similar way upon metallic solutions, precipitating the *selenides*.

There are two *chlorides of selenium*: the dichloride, Se_2Cl_2 a brown volatile liquid corresponding to dichloride of sulphur; and the tetrachloride, $SeCl_4$ a white crystalline solid, without any well-established analogue in the sulphur series.

Notwithstanding the resemblance between the two elements, there are two *sulphides of selenium*, a bisulphide (SeS_2) and a tersulphide (SeS_3). The former is obtained as a yellow precipitate when hydrosulphuric acid is passed into solution of selenious acid.

TELLURIUM.

Te = 129 parts by weight.

157. Tellurium (from *tellus, the earth*) is connected with selenium by analogies

stronger than those which connect that element with sulphur. It is even less frequently met with than selenium, being found chiefly in certain Transylvanian gold ores. It occasionally occurs in an uncombined form, but more frequently in combination with metals. Foliated or *graphic tellurium* is a black mineral containing the tellurides of lead, silver, and gold. Telluride of bismuth is also found in nature.

Tellurium is extracted from the foliated ore by a process similar to that for obtaining selenium. From telluride of bismuth it is procured by strongly heating the ore with a mixture of carbonate of potash and charcoal, when telluride of potassium is formed, which dissolves in water to a purple-red solution, from which tellurium is deposited on exposure to air.

Tellurium much more nearly resembles the metals than the non-metals in its physical properties, and is on that account often classed among the former, but it is not capable of forming a true basic oxide. In appearance it is very similar to bismuth (with which it is so frequently found), having a pinkish metallic lustre, and being, like that metal, crystalline and brittle. It fuses below a red heat, and is converted into a yellow vapour at a high temperature. When heated in air it burns with a blue flame edged with green, and emits fumes of tellurous acid (TeO_2) and a peculiar odour.

Like selenium, tellurium is dissolved by strong sulphuric acid, yielding a purple-red solution, from which water precipitates it unchanged.

The *oxides of tellurium* correspond in composition to those of selenium. *Tellurous acid* (TeO_2) is precipitated in the hydrated state when a solution of tellurium in diluted nitric acid is poured into water. If the nitric solution is boiled, a crystalline precipitate of anhydrous tellurous acid is obtained. Unlike selenious acid, tellurous acid is sparingly soluble in water. It is easily fusible, forming a yellow glass, which becomes white on cooling, and it may be sublimed unchanged. Its acid character is rather feeble, and with some of the stronger acids, it forms soluble compounds in which it takes the part of a very feeble base.

Telluric acid (TeO_3) is also a weak acid obtained by oxidising tellurium with nitre, precipitating the tellurate of potash with chloride of barium, and decomposing the tellurate of baryta with sulphuric acid. On evaporating the solution, crystals of hydrated telluric acid ($H_2O.TeO_3.2H_2O$) are obtained, which become $H_2O.TeO_3$ at a moderate heat, and when heated nearly to redness, are converted into an orange-yellow powder, which is the anhydrous acid. In this state it is insoluble in acids and alkalies. When strongly heated, it evolves oxygen, and becomes tellurous acid. The tellurates are unstable salts which are converted into tellurites when heated.

Telluretted hydrogen, or *hydrotelluric acid* (H_2Te), exhibits in the strongest manner the chemical analogy of tellurium with selenium and sulphur. It is a gas very similar to sulphuretted hydrogen in smell, and in most of its other properties. When its aqueous solution is exposed to the air, it yields a brown deposit of tellurium. When passed into metallic solutions it precipitates the tellurides.

The gas is prepared by decomposing telluride of zinc with hydrochloric acid.

The most characteristic property of tellurium compounds, is that of furnishing the purple solution of telluride of potassium, when fused with carbonate of potash and charcoal, and treated with water. Two solid *chlorides of tellurium* have been obtained; $TeCl_2$ is a black solid with a violet coloured vapour, and is decomposed by water into tellurium and $TeCl_4$. The latter may be obtained as a white crystalline volatile solid, decomposed by much water into hydrochloric and tellurous acids. There are also two *sulphides of tellurium* corresponding to the oxides, from which they may be obtained as dark brown precipitates, by the action of hydrosulphuric acid. They are both sulphur acids, and, therefore, soluble in alkaline sulphides.

158. *Review of the sulphur group of elements.*—The three elements—sulphur, selenium, and tellurium—exhibit a relation of a similar character to that observed between the members of the chlorine group, both in their physical and chemical properties.

Sulphur is a pale yellow solid, easily fusible and volatile, without any trace of metallic lustre, and of specific gravity 2·05 (sp. gr. of vapour, 2·23). Selenium is either a red powder or a lustrous mass appearing black, but transmitting red light through thin layers; much less fusible and volatile than sulphur, and of specific gravity 4·8 (sp. gr. of vapour, 5·68). Tellurium has a brilliant metallic lustre, is much less fusible and volatile than selenium, and of specific gravity 6·65 (sp. gr. of vapour, 9·0).

Sulphur (atomic weight 32) has the most powerful attraction for oxy-

gen, hydrogen, and the metals. Selenium (atomic weight 79·5) ranks next in the order of chemical energy. Tellurium (atomic weight 129) has a less powerful attraction for oxygen, hydrogen, and the metals, than either sulphur or selenium. This element appears to stand on neutral ground between the non-metallic bodies and the less electropositive metals.

Sulphur, selenium, and tellurium are diatomic or bivalent elements.

PHOSPHORUS.

P = 31 parts by weight.*

159. This is the only element for the ordinary preparation of which animal substances are employed. It is never known to occur uncombined in nature, but is found abundantly in the form of *phosphate of lime* ($3CaO.P_2O_5$), which is contained in the minerals *coprolite*, *phosphorite*, and *apatite*, and occurs diffused, though generally in small proportion, through all soils upon which plants will grow, for this substance is an essential constituent of the food of most plants, and especially of the cereal plants which form so large a proportion of the food of animals. The seeds of such plants are especially rich in the phosphates of lime and magnesia.

Animals feeding upon these plants still further accumulate the phosphoric acid, for it enters, chiefly in the form of phosphate of lime, into the composition of almost every solid and liquid in the animal body, and is especially abundant in the bones, which contain about three-fifths of their weight of phosphate of lime. It is from this source that our supply of phosphorus is chiefly derived.

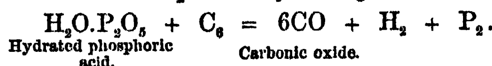
Composition of the Bones of Oxen.

Animal matter,	30·58
Phosphate of lime,	57·67
Fluoride of calcium,	2·69
Carbonate of lime,	6·99
Phosphate of magnesia,	2·07
	100·00

What is here termed animal matter is a cartilaginous substance, converted into gelatine when the bones are heated with water under pressure, and containing carbon, hydrogen, nitrogen, and oxygen. It was formerly the custom to get rid of this by burning the bones in an open fire, but the increased demand for chemical products, and the diminished supply of bones, have taught economy, so that the cartilaginous matter is now dissolved out by heating the bones with water at a high pressure for the manufacture of glue; or the bones are subjected to destructive distillation, so as to save the ammonia which they evolve, and the bone charcoal thus produced is used by the sugar-refiner until its decolorising powers are exhausted, when it is heated in contact with air to burn away the charcoal, and leave the *bone-ash*, consisting chiefly of phosphate of lime ($3CaO.P_2O_5$). In order to extract the phosphorus, the bone-ash is heated for some time with diluted sulphuric acid, which removes the greater part of the lime in the form of the sparingly soluble sulphate of lime, leaving

* The vapour of phosphorus is 62 times as heavy as hydrogen, so that its atom only occupies half a volume, if the atom of hydrogen be taken to occupy one volume.

the phosphoric acid in the solution, which is strained from the deposit, evaporated to a syrup, mixed with charcoal, thoroughly dried in an iron pot, and distilled in an earthen retort (fig. 217), when the carbon removes the oxygen from the phosphoric acid, and the phosphorus distils over, and is condensed in a receiver containing water to protect it from the action of the air. The decomposition of the dried phosphoric acid by the carbon of the charcoal is expressed by the equation—



$$\underset{\text{Hydrated phosphoric acid.}}{H_2O.P_2O_5} + C_6 = \underset{\text{Carbonic oxide.}}{6CO} + H_2 + P_2.$$

This is the simplest account that can be given of the preparation of phosphorus from bone-ash, but it is not strictly correct, for the sulphuric acid does not remove

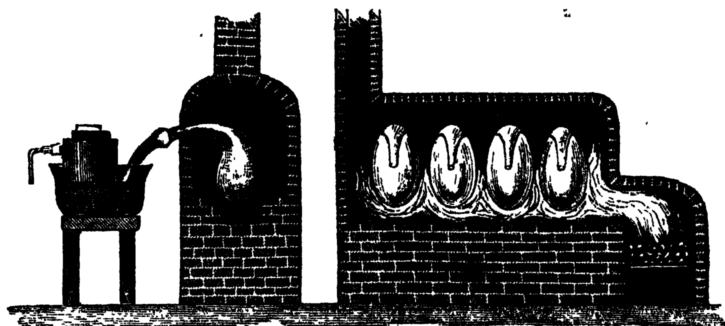
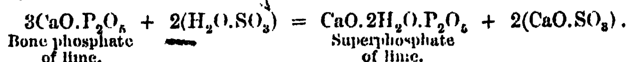


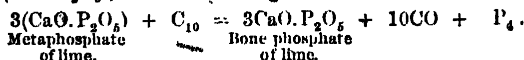
Fig. 217.—Extraction of phosphorus.

the whole of the lime from the phosphate, a portion remaining in the solution containing the phosphoric acid, so that this solution is generally said to contain *superphosphate of lime*, and the action of the sulphuric acid is thus represented—



$$\underset{\text{Bone phosphate of lime.}}{3CaO.P_2O_5} + 2(H_2O.SO_3) = \underset{\text{Superphosphate of lime.}}{CaO.2H_2O.P_2O_5} + 2(CaO.SO_3).$$

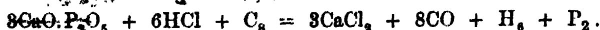
When the superphosphate of lime is dried, it becomes converted into *metaphosphate of lime* ($CaO.P_2O_5$), and on distilling this with charcoal—



$$\underset{\text{Metaphosphate of lime.}}{3(CaO.P_2O_5)} + C_{10} = \underset{\text{Bone phosphate of lime.}}{3CaO.P_2O_5} + 10CO + P_4.$$

Silicic acid (sand) is sometimes added to combine with the lime, and liberate the remainder of the phosphoric acid, so that it may be decomposed by the charcoal.

On the small scale, for the sake of illustration, phosphorus may be prepared by a process which has also been successfully employed for its manufacture in quantity, and consists in heating a mixture of bone-ash and charcoal in a stream of hydrochloric acid gas—



$$3CaO.P_2O_5 + 6HCl + C_8 = 3CaCl_2 + 8CO + H_6 + P_2.$$

A mixture of equal weights of well-dried charcoal and bone-ash, both in fine powder, is introduced into a porcelain tube sheathed with copper, and placed in a charcoal furnace (fig. 218). One end of the tube is connected with a flask (A), containing fused salt and sulphuric acid for evolving hydrochloric acid, and the other is cemented with putty into a bent retort neck (B), for conveying the phosphorus into a vessel of water (C). On heating the porcelain tube to bright redness, phosphorous distils over in abundance. The hydrogen and carbonic oxide inflame as they escape into the air, from their containing phosphorus vapour.

When first prepared, the phosphorus is red and opaque, from the presence of some suboxide of phosphorus and mechanical impurities; the latter are removed by melting the phosphorus under warm water, and

squeezing it through wash leather. The phosphorus is then fused under ammonia to remove any acid impurity, and afterwards under bichromate of potash acidified with sulphuric acid, when the chromic acid oxidises the suboxide of phosphorus, and converts it into phosphoric acid which dissolves. The phosphorus is then thoroughly washed, melted under water, and drawn up into glass tubes, where it solidifies into the sticks in which it is sold. These are always preserved under water from the action of oxygen, and in tin cases from that of light.

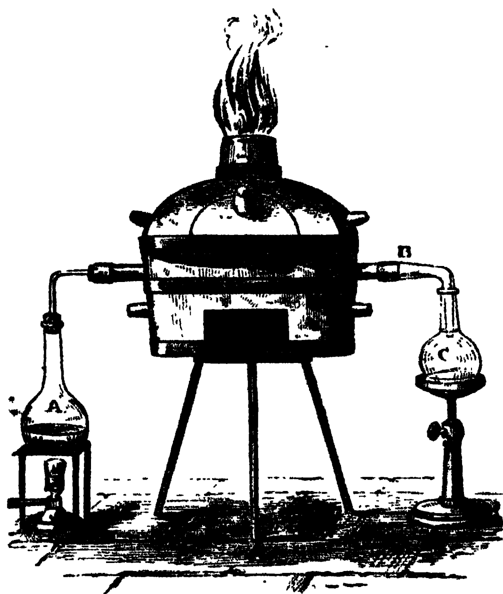


Fig. 218.

Pure ordinary phosphorus is almost colourless and transparent, but when exposed to light, and especially to direct sun-light, it gradually acquires an opaque red colour, from its partial conversion into the allotropic variety known as red or *amorphous phosphorus*. By tying bands of black cloth round a stick of phosphorus and exposing it, under water, to the action of sun-light, alternate zones of red may be produced.

Even though the phosphorus be screened from light, it will not remain unchanged unless the water be kept quite free from air, which irregularly corrodes the surface of the phosphorus, rendering it white and opaque. This action is accelerated by exposure to light.

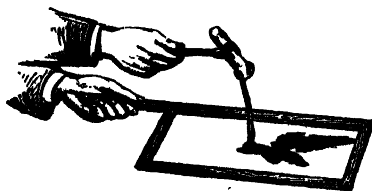
The most remarkable character of ordinary phosphorus is its easy inflammability. It inevitably takes fire in air when heated a little above its melting point (111°·5 F.), burning with a brilliant white flame, which becomes insupportable when the combustion takes place in oxygen (p. 23), and evolving dense white clouds of solid phosphoric acid. When a piece of dry phosphorus is exposed to the air, it combines slowly with oxygen, forming phosphorous acid,* and its temperature often becomes so much elevated during this slow combustion, that it melts and takes fire, especially if the combination be encouraged by the warmth of the hand or by friction. Hence, ordinary phosphorus must never be handled or cut in the dry state, but always under water, for it causes most painful burns.

The slow oxidation of phosphorus is attended with that peculiar luminous appearance which is termed *phosphorescence* (*φῶς, light, φέρω, to bear*), but this glow is not seen in pure oxygen or in air containing a minute proportion of olefiant gas or oil of turpentine. It will be remembered

* The white fumes evolved by phosphorus in moist air are said to consist partly of nitrate of ammonia, formed by the action of the ozonised oxygen upon the air and aqueous vapour.

that the slow oxidation of phosphorus is attended with the formation of ozone.

The characteristic behaviour of phosphorus in air is best observed when the phosphorus is in a finely-divided state. When a fragment of phosphorus is shaken with a little bisulphide of carbon, it is quickly dissolved, and if the solution be poured upon a piece of filtering-paper (fig. 219), and allowed to evaporate in a darkened room, the very thin film of phosphorus which is left will exhibit a glow increasing in brilliancy till the phosphorus bursts out into spontaneous combustion.

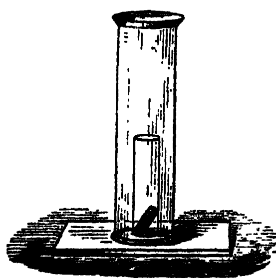

Fig. 219.

If phosphorus be dissolved in olive oil, at a gentle heat, the solution is strongly phosphorescent when shaken in a bottle containing air, or when rubbed upon the hands.

Characters may be written on paper with a stick of phosphorus held in a thickly-folded piece of damp paper (having a vessel of water at hand into which to plunge the phosphorus if it should take fire). When the paper is held with its back to the fire, or to a hot iron, in a darkened room, a twinkling combustion of the finely-divided phosphorus will ensue, and the letters will be burnt into the paper. Phosphorus, which has been partly oxidised, is even more easily inflamed than pure phosphorus. If a few small pieces of phosphorus be placed in a dry stoppered bottle, gently warmed till they melt, and then shaken round the sides of the bottle so as to become partly converted into red oxide of phosphorus, it will be found, long after the bottle is cold, to be spontaneously inflammable, so that if a wooden match tipped with sulphur be rubbed against it, the phosphorus which it takes up will ignite when the match is brought into the air, kindling the sulphur, which will inflame the wood. This was one of the earliest forms in which phosphorus was employed for the purpose of procuring an instantaneous light. If the stopper be greased, the phosphorus may be preserved unchanged for a long time.

In the last experiment, if the wood had not been tipped with sulphur, the phosphorus would not have kindled it, the flame of phosphorus generally being unable to ignite solid combustibles, because it deposits upon them a coating of phosphoric acid, which protects them from the action of air. Hence, in the manufacture of lucifer matches, the wood is first tipped with sulphur, or wax, or paraffine, which easily give off combustible vapours to be kindled by the flame of the phosphorus composition, and thus to inflame the wood.

If a small stick of phosphorus be carefully dried with filtering paper, and dropped into a cylinder of oxygen, which is afterwards covered with a glass plate, no luminosity will be observed in a darkened room until the cylinder is placed under the air-pump receiver, and the air slowly exhausted. When the oxygen has thus been rarefied to about one-fifth of its former density, the phosphorescence will be seen. A similar effect may be produced by covering the cylinder of oxygen containing the phosphorus (having removed the glass plate) with another cylinder, about four times its size (fig. 220), filled with carbonic acid, which will gradually dilute the oxygen and produce phosphorescence. By suspending—in a bottle of air containing a strongly luminous piece of phosphorus—a piece of paper with a drop of oil of turpentine upon it, the glow may be almost instantaneously destroyed. A small tube of olefiant gas or coal-gas dropped into the bottle will also extinguish the luminosity.


Fig. 220.

Ordinary phosphorus is slowly converted into vapour at the ordinary temperature, and emits in the air white fumes with a peculiar alliaceous smell, which appear phosphorescent in the dark. When heated out of contact with air, it boils at 550° F., and is converted into a colourless vapour.

The luminosity of phosphorus vapour is seen to advantage when a piece of phos-

phorus is boiled with water in a narrow-necked flask, or a test-tube with a cork and narrow tube. The steam charged with vapour of phosphorus has all the appearance of a blue flame in a darkened room, but of course combustibles are not inflamed by it, since its temperature is not higher than 212° F. Phosphorus may be distilled with perfect safety in an atmosphere of carbonic acid, the neck of the retort being allowed to dip under water in the receiver.

Although ordinary phosphorus is of a decidedly glassy or *vitreous* structure, and not at all crystalline, it may be obtained in dodecahedral crystals, by allowing its solution in bisulphide of carbon to evaporate in an atmosphere of carbonic acid.

The conversion of ordinary phosphorus into the red or *amorphous phosphorus* is one of the most striking instances of allotropic modification. When phosphorus is heated for a considerable length of time to about 450° F. *in vacuo*, or in an atmosphere in which it cannot burn, it becomes converted into a red infusible mass of amorphous phosphorus. This form of phosphorus differs as widely from the vitreous form as graphite differs from diamond. It is almost unchangeable in the air, evolves no vapour, is not luminous, cannot be inflamed by friction, or even by any heat short of 500° F., when it actually becomes reconverted into ordinary phosphorus.* Amorphous phosphorus is insoluble in the solvents for ordinary phosphorus. The two varieties also differ greatly in specific gravity, that of the ordinary phosphorus being 1·83, and of the amorphous variety 2·14.

The conversion of vitreous into amorphous phosphorus may be effected by heating it in a flask (A, fig. 221) placed in an oil-bath (B), maintained at a temperature ranging from 450° to 460° F., the flask being furnished with a bent tube (C) dipping into mercury, and with another tube (D) for supplying carbonic acid gas, dried by passing over chloride of calcium. The flask should be thoroughly filled with carbonic acid before applying heat, and the tube delivering it may then be closed with a small clamp (E). After exposure to heat for about forty hours, but little ordinary phosphorus will remain, and this may be removed by allowing the mass to remain in contact with bisulphide of carbon for some hours, and subsequently washing it with fresh bisulphide of carbon till the latter leaves no phosphorus when evaporated.

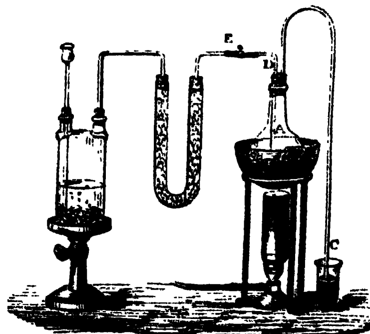


Fig. 221.

On the large scale, the red phosphorus is prepared by heating about 200 lbs. of vitreous phosphorus to 450° F. in an iron boiler. After three or four weeks the phosphorus is found to be converted into a hard red brittle mass, which is ground by mill-stones under water, and separated from the ordinary phosphorus either by bisulphide of carbon or caustic soda, in which the latter is soluble. The temperature requires careful regulation, for if it be allowed to rise to 500°, the red phosphorus quickly resumes the vitreous condition, evolving the heat which it had absorbed during its conversion, and thus converting much of the phosphorus into vapour. This reconversion may be shown by heating a little red phosphorus in a narrow test-tube, when drops of vitreous phosphorus condense on the cool part of the tube. The colour of different specimens of amorphous phosphorus varies considerably; that prepared on the large scale is usually of a dark purplish colour, but it may be obtained of a bright scarlet colour. Rhombohedral crystals of phosphorus, resembling crystals of arsenic in form and

* According to Hittorf, the reconversion does not take place till 800° F., the red phosphorus being convertible into vapour below that temperature, without fusion.

metallic appearance, have been obtained by fusing phosphorus with lead, and dissolving out the latter with diluted nitric acid (sp. gr. 1·1).

Ordinary phosphorus is very poisonous, whilst amorphous phosphorus appears to be harmless. The former is employed, mixed with fatty substances, for poisoning rats and beetles. Cases are, unhappily, not very rare, of children being poisoned by sucking the phosphorus composition on lucifer matches. The vapour of phosphorus also produces a very injurious effect upon the persons engaged in the manufacture of lucifer matches, resulting in the decay of the lower jaw-bone. This evil is much mitigated by good ventilation, or by diffusing turpentine vapour through the air of the work-room, and attempts have been made to obviate it entirely by substituting amorphous phosphorus for the ordinary variety, but, as might be expected, the matches thus made are not so sensitive to friction as those in which the vitreous phosphorus is used.

The difference between the two varieties of phosphorus, in respect to chemical energy, is seen when they are placed in contact with a little iodine on a plate, when the ordinary phosphorus undergoes combustion, and the red phosphorus remains unaltered.

Black phosphorus has been obtained by heating vitreous phosphorus to a little above its melting point and suddenly cooling it. It is reconverted by fusion and slow cooling. *Viscous phosphorus* results from the sudden cooling of phosphorus heated nearly to its boiling point.

Ordinary phosphorus is capable of direct union with oxygen, chlorine, bromine, iodine, sulphur, and most of the metals, with which it forms *phosphides* or *phosphurets*. Even gold and platinum unite with this element when heated, so that crucibles of these metals are liable to corrosion when heated in contact with a phosphate in the presence of a reducing agent, such as carbon. Thus the inside of a platinum dish or crucible is roughened when vegetable or animal substances containing phosphates are incinerated in it. The presence even of small quantities of phosphorus in metallic iron or copper produces considerable effect upon their physical qualities.

Phosphorus has the property, a very remarkable one in a non-metal, of precipitating some metals from their solutions in the metallic state. If a stick of phosphorus be placed in a solution of sulphate of copper, it becomes coated with metallic copper, the phosphorus appropriating the oxygen. This has been turned to advantage in copying very delicate objects by the electrotype process, for by exposing them to the action of a solution of phosphorus in ether or bisulphide of carbon, and afterwards to that of a solution of copper, they acquire the requisite conducting metallic film, even on their finest filaments. Solutions of silver and gold are reduced in a similar manner by phosphorus.

By floating very minute scales of ordinary phosphorus upon a dilute solution of chloride of gold, the metal will be reduced in the form of an extremely thin film, which may be raised upon a glass plate, and will be found to have various shades of green and violet by transmitted light, dependent upon its thickness, whilst its thickest part exhibits the ordinary colour of the metal to reflected light. By heating the films on the plate, various shades of amethyst and ruby are developed. If a very dilute solution of chloride of gold in distilled water be placed in a perfectly clean bottle, and a few drops of ether, in which phosphorus has been dissolved, poured into it, a beautiful ruby-coloured liquid is obtained, the colour of which is due to metallic gold in an extremely finely divided state, and on allowing it to stand for some months, the metal subsides as a purple powder, leaving the liquid colourless. If any saline impurity be present in the gold solution, the colour of the reduced gold will be amethyst or blue. These experiments (Faraday) illustrate very strik-

ingly the use of gold for imparting ruby and purple tints to glass and the glaze of porcelain.

160. *Lucifer matches* are made by tipping the wood with sulphur or wax or paraffine to convey the flame, and afterwards with the match composition, which is generally composed of saltpetre or chlorate of potash, phosphorus, red lead, and glue, and depends for its action on the easy inflammation, by friction, of phosphorus when mixed with oxidising agents like saltpetre (KNO_3), chlorate of potash ($KClO_3$), or red lead (Pb_3O_4), the glue only serving to bind the composition together and attach it to the wood. The composition used by different makers varies much in the nature and proportions of the ingredients. In this country, chlorate of potash is most commonly employed as the oxidising agent, such matches usually kindling with a slight detonation; but the German manufacturers prefer either nitrate of potash or nitrate of lead, together with binoxide of lead or with red lead, which produce *silent matches*.

Sulphide of antimony (which is inflamed by friction with chlorate of potash, see p. 163) is also used in those compositions in which a part of the phosphorus is employed in the amorphous form, and fine sand or powdered glass is very commonly added to increase the susceptibility of the mixture to inflammation by friction.

The match composition is coloured either with ultramarine blue, Prussian blue, or vermilion. In preparing the composition, the glue and the nitre or chlorate of potash are dissolved in hot water, the phosphorus then added and carefully stirred in until intimately mixed, the whole being kept at a temperature of about 100° F. The fine sand and colouring matter are then added, and when the mixture is complete, it is spread out upon a stone slab heated by steam, and the sulphured ends of the matches are dipped into it.

The *safety matches*, which refuse to ignite unless rubbed upon the bottom of the box, are tipped with a mixture of sulphide of antimony, chlorate of potash, and powdered glass, which is not sufficiently sensitive to be ignited by any ordinary friction, but inflames at once when rubbed upon the amorphous phosphorus mixed with glass which coats the rubber beneath the box. On this principle some French matches have been made which can be ignited only by breaking the match and rubbing the two ends together.

It would be very desirable to dispense entirely with the use of phosphorus in lucifer matches, not only because of the danger from accident and disease in the manufacture, but because a very large quantity of phosphate of lime which ought to be employed for agricultural purposes is now devoted to the preparation of phosphorus, of which six tons are said to be consumed annually in this country for the manufacture of matches. The most successful attempt in this direction appears to be the employment of a mixture of chlorate of potash and hyposulphite of lead, in place of the ordinary phosphorus composition.

For illustration, very excellent matches may be made upon the small scale in the following manner. The slips of wood are dipped in melted sulphur so as to acquire a slight coating. 30 grains of gelatine or isinglass are dissolved in 2 drachms of water in a porcelain dish placed upon a steam-bath; 20 grains of ordinary phosphorus are then added, and well mixed in with a piece of stick; to this mixture are added, in succession, 15 grains of red lead and 50 grains of powdered chlorate of potash. The sulphured matches are dipped into this paste, and left to dry in the air.

To make the safety matches: 10 grains of powdered chlorate of potash and 10 grains of sulphide of antimony are made into a paste with a few drops of a warm

solution of 20 grains gelatine in 2 drachms water, the sulphured matches being tipped with this composition. The rubber is prepared with 20 grains of amorphous phosphorus, and 10 grains of finely-powdered glass, mixed with the solution of gelatine, and painted on paper or card-board with a brush.

161. *Phosphorus-fuze composition.*—To ignite the Armstrong percussion shells, a very sensitive detonating composition is employed, which is composed of amorphous phosphorus, chlorate of potash, shellac, and powdered glass made into a paste with spirit of wine. This is placed in the little cap designed for it, and when dry is waterproofed with a little shellac dissolved in spirit.

Such a composition may be prepared *with care* in the following manner:—4 grains of powdered chlorate of potash are moistened on a plate with 6 drops of spirit of wine, 4 grains of powdered amorphous phosphorus are added, and the whole mixed at arm's length with a bone-knife, avoiding great pressure. The mixture, which should still be quite moist, is spread in small portions upon ten or twelve pieces of filtering paper, and left in a safe place to dry. If one of these be gently pressed with a stick, it explodes with great violence. It is dangerous to press it with the blade of a knife, as the latter is commonly broken, and the pieces projected with considerable force. A stick dipped in oil of vitriol of course explodes it immediately. If a bullet be placed very lightly upon one of the pellets, and the paper tenderly wrapped round it, a percussion shell may be extemporised, which explodes with a loud report when dropped upon the floor.

Oxides of Phosphorus.

162. There are only two compounds of phosphorus with oxygen which have been obtained and satisfactorily examined in the separate state, viz., *phosphorous acid* (P_2O_3), and *phosphoric acid* (P_2O_5). The *sub-oxide of phosphorus* (P_4O) is said to have been obtained, but very little is known of it.

Oxides of Phosphorus.

Name.	Formula.	By Weight.	
		Phosphorus.	Oxygen.
Suboxide of phosphorus?	P_4O	124	16
Phosphorous acid	P_2O_3	62	48
Phosphoric acid	P_2O_5	62	80

Phosphoric Acid.

P_2O_5 = 142 parts by weight.

163. Phosphoric acid is by far the most important of the compounds of phosphorus. It has been already noticed as almost the only form of combination in which that element is met with in nature, and as an indispensable ingredient in the food of plants and animals. No other mineral substance can bear comparison with it as a measure of the capability of a country to support animal life. The acid itself is very useful in calico-printing and some other arts.

The mineral sources of this acid appear to be *phosphorite*, *coprolite*, and *apatite*, all consisting essentially of phosphate of lime ($3CaO.P_2O_5$), but associated in each case with fluoride of calcium, which is also contained, with phosphate of lime, in bones, and would appear to indicate an organic origin for these minerals. Phosphorite is an earthy-looking substance,

forming large deposits in Estremadura. Apatite (from ἀπατάω, *to cheat*, in allusion to mistakes in its early analysis) occurs in prismatic crystals, and is met with in the Cornish tin-veins. Both these minerals are largely imported from Spain, Norway, and America, for use in this country as a manure.

Coprolites (κόπρος, *dung*, λίθος, *a stone*, from the idea that they were petrified dung) are rounded nodules of phosphate of lime, which are found abundantly in this country.

Large quantities of phosphoric acid, combined with lime and magnesia, are imported in the form of *guano*, the partially decomposed excrement of sea-fowl, which sometimes contains one-fourth of its weight of phosphoric acid.

Bones, however, must be regarded as the chief immediate source whence the phosphate of lime for agricultural purposes is derived.

Hydrated phosphoric acid is obtained from bone-ash by decomposing it with sulphuric acid, so as to remove as much of the lime as possible in the form of sulphate, which is strained off, and the acid liquid neutralised with carbonate of ammonia, which precipitates any unchanged phosphate of lime, and converts the phosphoric acid into phosphate of ammonia, consisting of phosphoric acid, water, and ammonia. On evaporating the solution, and heating the phosphate of ammonia, the ammonia is expelled, and hydrated phosphoric acid ($H_2O.P_2O_5$) is left in a fused state, solidifying to a glass on cooling. Thus prepared, however, it always retains some ammonia, and is contaminated with soda derived from the bones.

The pure hydrated acid is prepared by oxidising phosphorus with diluted nitric acid (sp. gr. 1·2), and evaporating the solution in a platinum dish, until the hydrated phosphoric acid begins to volatilise in white fumes—



$$5(H_2O.N_2O_5) + P_6 = 3(H_2O.P_2O_5) + 2H_2O + 10NO.$$

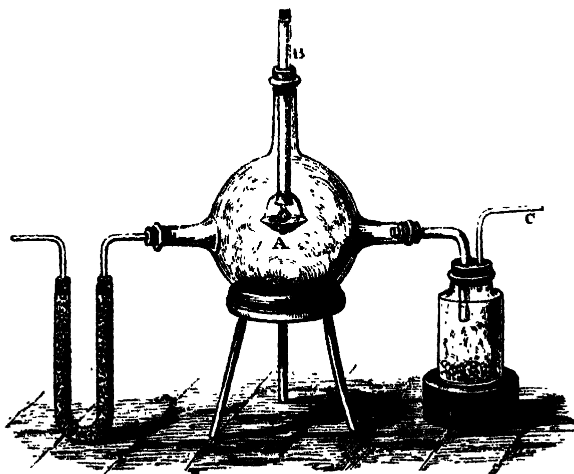


Fig. 222.

Some phosphorous acid is formed at an intermediate stage. A transparent glass (*glacial phosphoric acid*) is thus obtained, which eagerly absorbs moisture from the air, and becomes liquid.

The water cannot be separated from the hydrated phosphoric acid by the action of heat, so that the *anhydrous phosphoric acid* must be prepared by burning phosphorus in dry air.

When required in considerable quantity, the anhydrous phosphoric acid (*phosphoric anhydride*) is prepared by burning the phosphorus in a small porcelain dish (A. fig. 222) attached to a wide glass tube (B) for introducing the phosphorus, and suspended in a glass flask with two lateral necks, one of which is connected with a tube containing pumice-stone and oil of vitriol for drying the air as it enters, whilst the other neck is provided with a wide tube conveying the anhydrous phosphoric acid into a bottle connected, at C, with an aspirator, or cistern of water, for drawing air through the apparatus. The first piece of phosphorus is kindled by passing a hot wire down the wide tube, but afterwards the heat of the dish will always ignite the fresh piece as it is dropped in. The wide tube must be closed with a cork whilst the phosphorus is burning.



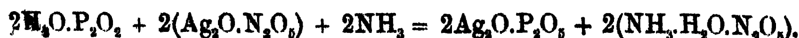
Fig. 223.

A small quantity of anhydrous phosphoric acid is more conveniently prepared by burning phosphorus under a large bell-jar of air, under which a shallow dish of oil of vitriol has been standing for an hour or two to dry the air. This dish is carefully removed without disturbing the air within the jar, and the well-dried phosphorus is introduced in a small porcelain crucible standing upon a large glass plate. The phosphorus having been kindled with a hot wire, the flakes of phosphoric acid will be seen falling like snow on to the glass plate, where they accumulate in a layer of considerable thickness. To preserve it, the phosphoric acid must be immediately scraped up with a bone or platinum knife and thrown into a thoroughly dry stoppered bottle.

Anhydrous phosphoric acid may be fused at a very high temperature, and even sublimed. Its great feature is its attraction for water; left exposed to the air for a very short time, it deliquesces entirely, becoming converted into hydrated phosphoric acid. It is often used by chemists as a *dehydrating agent*, and will even remove the water from oil of vitriol. When thrown into water, it hisses like a red-hot iron, but does not entirely dissolve at once, a few flakes of hydrated phosphoric acid remaining suspended in the liquid for some time. Phosphoric acid, like sulphuric acid, forms three definite combinations with water, but in the case of phosphoric acid, each of these three hydrates is a different acid, capable of producing different salts, whereas the sulphuric acid generates the same salts in whatever degree of hydration it is employed.

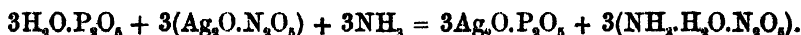
The solution obtained by dissolving anhydrous phosphoric acid in water contains *monohydrated phosphoric acid* or *metaphosphoric acid* ($H_2O.P_2O_5$). If a little nitrate of silver be added to a portion of it, a transparent gelatinous precipitate is formed, which is the metaphosphate of silver ($Ag_2O.N_2O_5 + H_2O.P_2O_5 = H_2O.N_2O_5 + Ag_2O.P_2O_5$).

If the solution of metaphosphoric acid be heated in a flask for a short time, it will lose the property of yielding a precipitate with nitrate of silver, unless one or two drops of ammonia be added to neutralise it, when an opaque white precipitate of pyrophosphate of silver ($2Ag_2O.P_2O_5$) is obtained, for the phosphoric acid has now been converted into the *dihydrated* or *pyrophosphoric acid* ($2H_2O.P_2O_5$). The formation of the precipitate is thus expressed—



$$2H_2O.P_2O_5 + 2(Ag_2O.N_2O_5) + 2NH_3 = 2Ag_2O.P_2O_5 + 2(NH_3.H_2O.N_2O_5).$$

When the solution of pyrophosphoric acid is mixed with more water and boiled for a long time, it gives, when tested with nitrate of silver and a little ammonia, a yellow precipitate of triphosphate of silver ($3Ag_2O.P_2O_5$); the phosphoric acid having become converted into *tri-hydrated* phosphoric acid ($3H_2O.P_2O_5$), and acting upon the nitrate of silver in the presence of ammonia, thus—



$$3H_2O.P_2O_5 + 3(Ag_2O.N_2O_5) + 3NH_3 = 3Ag_2O.P_2O_5 + 3(NH_3.H_2O.N_2O_5).$$

The *pyrophosphoric acid* ($2H_2O.P_2O_5$) cannot be obtained by the above process without an admixture of one of the other hydrates, but it has been obtained in crystals by decomposing the pyrophosphate of lead ($2PbO.P_2O_5$) with hydrosulphuric acid, and evaporating the filtered solution *in vacuo* over oil of vitriol.

Trihydrated phosphoric acid may also be obtained in prismatic crystals, by evaporating its solution in a similar way. This acid is also called *ortho-phosphoric acid* (ὀρθὸς, *true*), and *common* phosphoric acid, in allusion to the circumstance that the phosphates commonly met with and employed in the arts are the salts of this acid.

For it will be perceived that each of these acids is able to combine with a quantity of base equivalent to the water present in the hydrate. Thus the metaphosphoric acid ($H_2O.P_2O_5$) forms salts with one molecule of a base having the general formula M_2O, as in metaphosphate of soda, $Na_2O.P_2O_5$. Pyrophosphoric acid ($2H_2O.P_2O_5$) forms salts with three molecules, as in triphosphate (or subphosphate) of soda, $3Na_2O.P_2O_5$.

In the cases of pyrophosphoric and common phosphoric acids, it is not necessary that the two or three molecules of water should be displaced by the same base, for it is found that salts of these acids may be formed which contain two bases, and some in which part of the water does duty as a base. Examples of this kind are, the common phosphate of soda, $2Na_2O.H_2O.P_2O_5$, which is derived from the acid, $3H_2O.P_2O_5$, by the displacement of two molecules of water by soda; *microcosmic salt*, or phosphate of soda and ammonia, $Na_2O.(NH_4)_2O.H_2O.P_2O_5$, where two molecules of the water in the acid are displaced respectively by soda and by the imaginary oxide of ammonium $(NH_4)_2O$. A pyrophosphate of soda having the composition of $Na_2O.H_2O.P_2O_5$ may be prepared, and is obviously derived from the acid, $2H_2O.P_2O_5$, by the displacement of one molecule of water by soda.

It is evident that when water or ammonia enters into the composition of the salt, the action of heat may convert an ortho-phosphate into a pyrophosphate, or even into a metaphosphate.

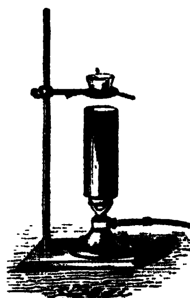


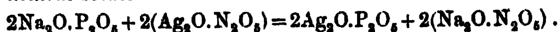
Fig. 224.

Thus, if a crystal of the common rhombic phosphate of soda ($2Na_2O.H_2O.P_2O_5.24Aq.$) be heated gently in a crucible (fig. 224), it melts in its water of crystallisation, and gradually dries up to a white mass, the composition of which, if not heated beyond 300° F., will be $2Na_2O.H_2O.P_2O_5$. If a little of this white mass be dissolved in water, the solution will be *alkaline* to red litmus paper; and if nitrate of silver (itself *neutral* to test-papers) be added to it, a *yellow* precipitate of triphosphate of silver will be obtained, and the solution will become strongly *acid*—



$$2Na_2O.H_2O.P_2O_5 + 3(Ag_2O.N_2O_5) = 3Ag_2O.P_2O_5 + 2(Na_2O.N_2O_5) + H_2O.N_2O_5$$

If the dried phosphate of soda be now strongly heated over a lamp, it will lose its basic water, and become pyrophosphate of soda (πῦρ, *fire*). On dissolving this in water, the solution will be *alkaline*, and will give with nitrate of silver a *white* precipitate and a *neutral* solution—



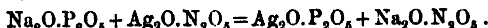
$$2Na_2O.P_2O_5 + 2(Ag_2O.N_2O_5) = 2Ag_2O.P_2O_5 + 2(Na_2O.N_2O_5).$$

Microcosmic salt ($Na_2O.(NH_4)_2O.H_2O.P_2O_5.8Aq.$), when dissolved in water, yields an *alkaline* solution which gives a *yellow* precipitate with nitrate of silver, the liquid becoming *acid*—



$$Na_2O(NH_4)_2O.H_2O.P_2O_5 + 3(Ag_2O.N_2O_5) = 3Ag_2O.P_2O_5 + Na_2O.N_2O_5 + (NH_4)_2O.N_2O_5 + H_2O.N_2O_5$$

But if the salt be heated in a crucible, it fuses, evolving water and ammonia, and leaving a transparent glass of metaphosphate of soda ($Na_2O.P_2O_5$), which may be dissolved by soaking in water, yielding a slightly *acid* solution, which gives a *white* gelatinous precipitate with nitrate of silver, the liquid being *neutral*—



$$Na_2O.P_2O_5 + Ag_2O.N_2O_5 = Ag_2O.P_2O_5 + Na_2O.N_2O_5.$$

The crystallised metaphosphate of soda retains 1 molecule of water when dried at 212° F., becoming $Na_2O.P_2O_5.H_2O$. On heating this to 300° F., the salt is converted into the acid pyrophosphate of soda, $Na_2O.H_2O.P_2O_5$, the water having assumed a basic character in the salt.

All the phosphates may be converted into tribasic phosphates, by fusing them with an alkaline hydrate or carbonate.*

164. *Phosphorous acid* (P_2O_3) is the product of the slow combustion of phosphorus. If a piece of phosphorus be heated in a long glass tube, into which a very slow current of dry air is drawn through a very narrow tube, it burns with a pale blue flame, and white flakes of anhydrous phosphorous acid are deposited. Phosphorous acid is more easily converted into vapour than phosphoric acid. It eagerly absorbs moisture from the air, and is decomposed when strongly heated in a sealed tube, yielding free phosphorus and phosphoric acid; $5P_2O_3 = 3P_2O_5 + P_4$.

Hydrated phosphorous acid is obtained in solution, mixed with phosphoric acid, when sticks of phosphorus arranged in separate tubes, open at both ends, and placed in a funnel over a bottle, are exposed under a bell-jar, open at the top, to air saturated with aqueous vapour. To obtain the pure acid, chlorine is very slowly passed through phosphorus fused under water, when the terchloride of phosphorus first formed is decomposed by the water into phosphorous and hydrochloric acids; $2PCl_3 + 6H_2O = 3H_2O.P_2O_3 + 6HCl$. The hydrochloric acid is expelled by a moderate heat, when the hydrated phosphorous acid is deposited in prismatic crystals. The water cannot be separated from phosphorous acid by heat; when the hydrate is heated, it is decomposed into hydrated phosphoric acid and gaseous phosphuretted hydrogen; $4(3H_2O.P_2O_3) = 3(3H_2O.P_2O_5) + 2PH_3$.

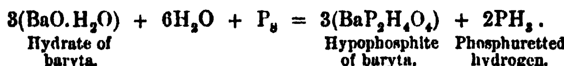
Solution of phosphorous acid gradually absorbs oxygen from the air, becoming phosphoric acid. This tendency to absorb oxygen causes it to act as a reducing agent upon many solutions; thus it precipitates finely-divided metallic silver from a solution of the nitrate, by which its presence may be recognised in the water in which ordinary phosphorus has been kept. The solution of phosphorous acid even reduces sulphurous acid, producing sulphuretted hydrogen and sulphur, the latter being formed by the action of the sulphuretted hydrogen upon the sulphurous acid; $2SO_2 + 2H_2O + 3(3H_2O.P_2O_3) = 2H_2S + 3(3H_2O.P_2O_5)$.

If solution of phosphorous acid be poured into a hydrogen apparatus, some phosphuretted hydrogen is formed which imparts a fine green tint to the hydrogen flame. When solution of phosphorous acid is mixed with a slight excess of solution of soda, and carefully evaporated, crystals are deposited which have the composition $2Na_2O.P_2O_3.11H_2O$. From these crystals, however, only 10 molecules of water can be separated, even at 570° F., leading to the belief that the elements of the last molecule of water really belong to the acid itself, and that the true formula of the phosphite of soda dried at that temperature is $2Na_2O.H_2O.P_2O_3$, or Na_2PHO_3. If this view be correct, phosphorous acid should form two classes of salts; accordingly, we find the acid phosphites containing only one molecule of base, the absent molecule being represented by water. Thus, acid phosphite of baryta dried at 212° F. has the composition $BaO.2H_2O.P_2O_3$, or $BaP_2H_4O_6$. When heated, the phosphites are converted into phosphates at the expense of the oxygen of the water contained

* It has been remarked that the *pliancy* of the acid character of phosphoric acid particularly fits it to take part in the vital phenomena. It may be regarded as three acids in one.

in them, the hydrogen being evolved, often accompanied by phosphuretted hydrogen.

165. *Hypophosphorous acid.*—When phosphorus is boiled with hydrate of baryta and water, the latter is decomposed, its hydrogen combining with part of the phosphorus to form phosphuretted hydrogen (spontaneously inflammable), which escapes, whilst the oxygen of the water unites with another part of the phosphorus, forming hypophosphorous acid, which combines with baryta and water to form hypophosphite of baryta; this may be obtained by evaporating the solution, in crystals having the composition $BaP_2H_4O_4$. The action of phosphorus upon hydrate of baryta may be represented by the equation—



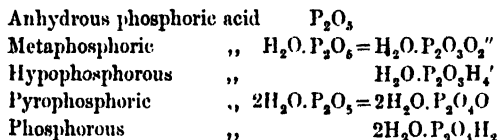
$$\underset{\text{Hydrate of baryta.}}{3(BaO.H_2O)} + 6H_2O + P_8 = \underset{\text{Hypophosphite of baryta.}}{3(BaP_2H_4O_4)} + \underset{\text{Phosphuretted hydrogen.}}{2PH_3}.$$

Some phosphate of baryta ($3BaO.P_2O_5$) is also formed at the same time, as the result of a secondary action.

By dissolving the hypophosphite of baryta in water, and decomposing it with the requisite quantity of sulphuric acid, so as to precipitate the baryta as sulphate, a solution is obtained which may be concentrated by careful evaporation till it has the composition represented by the formula $H_2P_2H_4O_4$. If this hydrated hypophosphorous acid be heated, it evolves phosphuretted hydrogen, and becomes converted into hydrated phosphoric acid; $2(H_2P_2H_4O_4) = 3H_2O.P_2O_5 + 2PH_3$. When exposed to the air it absorbs oxygen, and becomes converted into phosphorous and phosphoric acids. It is a more powerful reducing agent than phosphorous acid. The latter acid does not reduce a solution of sulphate of copper, but hypophosphorous acid when gently warmed with it, gives a black precipitate of *hydride of copper* (CuH), which is decomposed by boiling, evolving hydrogen and leaving metallic copper.

When heated, the hypophosphites evolve phosphuretted hydrogen, and are converted into phosphates. The hypophosphite of soda ($Na_2P_2H_4O_4$) is sometimes used in medicine; its solution has been known to explode with great violence during evaporation, probably from a sudden disengagement of phosphuretted hydrogen.

The phosphorous and hypophosphorous acids may be connected with phosphoric acid in the following manner—



Anhydrous phosphoric acid		P_2O_5
Metaphosphoric	,,	$H_2O.P_2O_5 = H_2O.P_2O_3O_2''$
Hypophosphorous	,,	$H_2O.P_2O_3H_4'$
Pyrophosphoric	,,	$2H_2O.P_2O_5 = 2H_2O.P_2O_4O$
Phosphorous	,,	$2H_2O.P_2O_4H_2$

where hypophosphorous acid is derived from metaphosphoric acid by displacing two atoms of diatomic oxygen by four atoms of monatomic hydrogen; and phosphorous acid is derived from pyrophosphoric acid by displacing one atom of diatomic oxygen by two atoms of monatomic oxygen.

166. *Suboxide of phosphorus* is supposed to constitute the yellow or red residue which is left in the dish when phosphorus burns in air, but it is always mixed with much phosphoric acid. If phosphorus be melted under water in a flask (fig. 225), and oxygen gas be allowed to bubble through it (a brass tube being employed to convey the oxygen), each bubble of the gas produces a brilliant flash, and the phosphorus is converted into red flakes, which were believed to be suboxide of phosphorus, but are really amorphous phosphorus. The true suboxide of phosphorus (P_4O) appears to be formed when small pieces of phosphorus are covered with terchloride of phosphorus, exposed to the air, and afterwards heated with water, when the suboxide is deposited as a yellow powder, becoming red at high temperatures, and inflaming when heated in air.

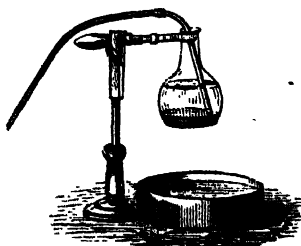


Fig. 225.

Phosphides of Hydrogen.

167. Although phosphorus and hydrogen do not combine directly, there are three compounds of these elements producible by processes of substitution, the composition of which is shown in the following table :—

Name.	Formula.	By Weight.	
		Phosphorus.	Hydrogen.
Phosphuretted hydrogen gas . .	PH_3	31	3
Liquid phosphide of hydrogen . .	PH_2	31	2
Solid phosphide	P_2H ?	62	1

Phosphuretted hydrogen gas (PH_3 = 34 parts by weight = 2 vols. = ½ vol. P + 3 vols. H) is by far the most important of these. It has been mentioned above as resulting from the action of heat upon hydrated phosphorous acid, and when prepared by this process it is obtained as a colourless gas, with a most powerful odour of putrid fish, inflaming on the approach of a light, and burning with a brilliant white flame, producing thick clouds of phosphoric acid. It is slightly heavier than air (sp. gr. 1·19), and has been liquefied under high pressure.

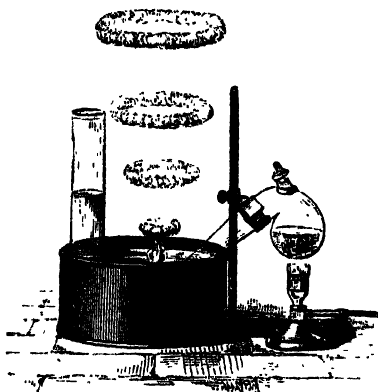


Fig. 226.—Preparation of phosphuretted hydrogen.

The ordinary method of preparing this gas for experimental purposes consists in boiling phosphorus with a strong solution of potash, when water is decomposed, its hydrogen combining with one part of the phosphorus, and its oxygen with another part forming hypophosphorous acid, which unites with the potash.

A few fragments of phosphorus are introduced into a small retort (fig. 226), which is then nearly filled with a strong solution of potash (sp. gr. 1·3*), and heated. The extremity of the neck of the retort should not be plunged under water until the spontaneously inflammable gas is seen burning at the orifice, and the retort must not be placed close to the face of the operator, since explosions sometimes take place in preparing the gas, and the boiling potash produces dangerous effects. The gas may be collected in small jars filled with water, taking care that no bubble of air is left in them. It contains phosphuretted hydrogen, mixed with free hydrogen, the latter being formed from the deoxidation of water by the hypophosphite of potash. As each bubble of this gas escapes into the air through the water of the pneumatic trough, it burns with a vivid white flame, producing beautiful wreaths of smoke (phosphoric acid), resembling the *gunner's rings* sometimes seen in firing cannon. Small bubbles sometimes escape without spontaneously inflaming. If a bubble be sent up into a jar of oxygen, the flash of light is extremely vivid, and the jar must be a strong one to resist the concussion. It is advisable to add a trace of chlorine to the oxygen to insure the inflammation of each bubble, for an accumulation of the gas would shatter the jar.

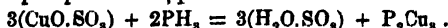
If this gas be passed through a tube cooled in a freezing mixture of ice and salt, the gas escaping from the tube is found to have lost its spontaneous inflammability,

* 450 grains of common stick potash dissolved in 1000 grains of water.

although it takes fire on contact with flame. The cold tube contains the *liquid phosphide of hydrogen* (PH_2), which was present in the gas in the state of vapour, and caused its spontaneous inflammability, for as soon as this liquid comes in contact with air it takes fire. When exposed to light, the liquid phosphide is decomposed into phosphuretted hydrogen gas and a yellow *solid phosphide* (P_2H), which is not spontaneously inflammable; $5PH_2 = P_2H + 3PH_3$. It is for this reason that the spontaneously inflammable gas loses that property when kept (unless in the dark), depositing the solid phosphide upon the sides of the jar.

By passing a few drops of oil of turpentine up through the water into a jar of the spontaneously inflammable gas, this property will be entirely destroyed, whereas the addition of a trace of nitrous acid imparts spontaneous inflammability.

Phosphuretted hydrogen, when passed through solutions of some of the metals, precipitates their phosphides. For example, with sulphate of copper it gives a black precipitate of phosphide of copper—



$$3(CuO.SO_3) + 2PH_3 = 3(H_2O.SO_3) + P_2Cu_3 .$$

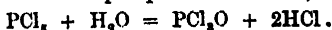
When this black precipitate is heated with solution of cyanide of potassium, it evolves self lighting phosphuretted hydrogen.* In fact this is one of the easiest and safest methods of preparing this gas; for the phosphide of copper is readily obtained by simply boiling phosphorus in a solution of sulphate of copper.

Phosphuretted hydrogen has great pretensions to rank as the chemical analogue of ammonia, for although it has no alkaline properties, it is capable of combining with hydrobromic and hydriodic acids to form crystalline compounds analogous to the hydrobromate and hydriodate of ammonia; these compounds, however, are decomposed by water. It will be seen hereafter, that when the hydrogen of phosphuretted hydrogen is displaced by certain compound radicals, such as ethyle, powerful organic bases are produced.

The spontaneously inflammable phosphuretted hydrogen may also be obtained by throwing fragments of *phosphide of calcium* into water; this substance is prepared by passing vapour of phosphorus over red-hot quick-lime, or simply by heating small lumps of quick-lime to bright redness in a crucible and throwing in fragments of phosphorus, closing the crucible immediately. The dark brown mass thus obtained is a mixture of pyrophosphate of lime and phosphide of calcium, of somewhat variable composition.

When phosphuretted hydrogen gas is decomposed by a succession of electric sparks, 2 vols. of the gas yield 3 vols. of hydrogen, the phosphorus being deposited in the red or amorphous form.

168. *Two chlorides of phosphorus* are known. The *terchloride* (PCl_3) is prepared by acting upon phosphorus with perfectly dry chlorine in the apparatus employed (p. 220) for preparing the chloride of sulphur. Terchloride of phosphorus distils over very easily (boiling point, 173°·4 F.), as a colourless pungent liquid (sp. gr. 1·62), which fumes strongly in air, its vapour decomposing the moisture of the air and producing hydrochloric acid fumes. In contact with water the liquid is immediately decomposed, yielding hydrochloric and phosphorous acids, as described for the preparation of the latter acid (p. 234). Its analogy to anhydrous phosphorous acid is shown by its absorbing oxygen when boiled in the presence of that gas, and forming the *oxychloride of phosphorus* (PCl_3O) corresponding in composition to anhydrous phosphoric acid. It also absorbs chlorine with avidity, becoming converted into *pentachloride of phosphorus* (PCl_5). This compound, however, is more conveniently prepared by passing chlorine through a solution of phosphorus in bisulphide of carbon, carefully cooled. On evaporation, the pentachloride of phosphorus is deposited in white prismatic crystals, which volatilise below 212° F., and fume when exposed to air, from the production of hydrochloric acid. When thrown into water it is decomposed into phosphoric and hydrochloric acids; $2PCl_5 + 8H_2O = 3H_2O.P_2O_5 + 10HCl$. But if it be allowed to deliquesce in air, only a partial decomposition takes place, and the oxychloride of phosphorus is formed;



$$PCl_5 + H_2O = PCl_3O + 2HCl .$$

This oxychloride of phosphorus may also be produced by heating pentachloride of phosphorus with anhydrous phosphoric acid; $P_2O_5 + 3PCl_5 = 5PCl_3O$. A more instructive method of preparing it consists in distilling the pentachloride of phosphorus with crystallised boracic acid—



$$3PCl_5 + 3H_2O.B_2O_3 = 3PCl_3O + 6HCl + B_2O_3 .$$

* Cyanide of copper and phosphide of potassium being formed, and the latter decomposed by water, giving phosphuretted hydrogen, and hypophosphite of potash.

Some of the hydrated organic acids (succinic, for example) may be obtained in the anhydrous state, as the boracic acid is in this case, by distillation with pentachloride of phosphorus. The oxychloride of phosphorus distils over (boiling point, 230° F.) as a heavy (sp. gr. 1·7) colourless fuming liquid of pungent odour. Of course it is decomposed by water, yielding hydrochloric and phosphoric acids. It will be found of the greatest use in effecting certain transformations in organic substances.

The analogy between water and hydrosulphuric acid would lead to the expectation that a *sulphochloride of phosphorus* (PCl_3S), corresponding to the oxychloride, would be formed by the action of hydrosulphuric acid upon pentachloride of phosphorus; $PCl_5 + H_2S = PCl_3S + 2HCl$. It is a colourless fuming liquid, which is slowly decomposed by water, giving phosphoric, hydrochloric, and hydrosulphuric acids; $2PCl_3S + 8H_2O = 3H_2O.P_2O_5 + 6HCl + 2H_2S$. When acted on by solution of soda, the sulphochloride of phosphorus loses its chlorine to the sodium, and acquires an equivalent quantity of oxygen, a *sulphoxy-phosphate* of soda ($3Na_2O.P_2O_3S_2.24H_2O$) being deposited in crystals. This salt evidently corresponds in composition to the triphosphate of soda ($3Na_2O.P_2O_5.24H_2O$), and its production is expressed by the equation; $2PCl_3S + 6Na_2O = 6NaCl + 3Na_2O.P_2O_3S_2$. Salts of similar composition may be obtained with other metallic oxides.

The *bromides* and *oxybromide of phosphorus* correspond to the chlorine compounds.

Iodine in the solid state combines very energetically with phosphorus, but if the two elements be brought together in a state of solution in bisulphide of carbon, a more moderate action ensues, and two *iodides of phosphorus* may be obtained in crystals; a teriodide (PI_3) corresponding to the terchloride, and a biniodide (PI_2), which has no analogue either among the oxygen, chlorine, or bromine compounds of phosphorus.

The addition of a very small quantity of iodine to ordinary phosphorus, fused in a flask filled with carbonic acid gas, materially accelerates its conversion into the red modification, and allows the change to be effected at a much lower temperature than that required when the phosphorus is heated alone. This has been ascribed to the disposition of the electro-negative iodine to cause the phosphorus to assume the positive or amorphous state when entering into combination with it; this compound being decomposed by heat with separation of amorphous phosphorus, the iodine combines with a fresh portion of the phosphorous, which is converted in the same way.

169. The *sulphides of phosphorus* may be formed by the direct combination of their elements. If ordinary phosphorus be used, the experiment is not unattended with danger, and should be performed under water. It is safer to combine the amorphous phosphorus with sulphur, at a moderate heat, in an atmosphere of carbonic acid.

There appear to be at least three sulphides of phosphorus, viz., the protosulphide (P_2S), the sesquisulphide (P_2S_3), representing phosphorous acid (P_2O_3), and the pentasulphide (P_2S_5), analogous to phosphoric acid (P_2O_5).

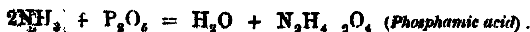
P_2S is a yellow oily liquid which may be distilled out of contact with air.

P_2S_3 is a yellow solid, easily fusible, and capable of subliming in a crystalline form if air be excluded. It may be produced by the action of hydrosulphuric acid upon terchloride of phosphorus; $2PCl_3 + 3H_2S = P_2S_3 + 6HCl$.

P_2S_5 crystallises more readily in a fused state than P_2S_3. Both these sulphides, unlike the protosulphide, are easily decomposed by water. All the sulphides are sulphur-acids.

170. *Action of ammonia upon anhydrous phosphoric acid.*—Some remarkably stable and definite compounds, containing nitrogen and phosphorus, are derived from the action of ammonia on anhydrous phosphoric acid, and the study of their mode of formation will be found to throw some light upon the history of a very large and important class of organic substances known as the *amides.*

Anhydrous phosphoric acid absorbs ammoniacal gas with great evolution of heat, and produces, not phosphate of ammonia, for that cannot be formed unless water is present, but the ammoniacal salt of a new acid, *phosphamic acid*, which contains the elements of acid phosphate of ammonia ($(NH_4)_2O.2H_2O.P_2O_5$) *minus* four molecules of water—



$$2NH_3 + P_2O_5 = H_2O + N_2H_4\,{}_2O_4 \text{ (Phosphamic acid)}.$$

When gently heated with water, phosphamic acid is converted into acid phosphate of ammonia.

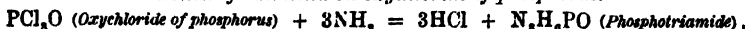
When the phosphamate of ammonia is heated in a current of dry ammonia, it gives off water, and leaves a yellow insoluble substance formerly supposed to be *phosphide of nitrogen*, but now known as *phospham*—



$$2NH_3.H_2O.N_2H_4P_2O_4 \text{ (Phosphamate of ammonia)} = 5H_2O + 2N_2HP \text{ (Phospham)}.$$

It is not surprising that the presence of hydrogen in this substance should have been overlooked, for it may be heated to redness (out of contact with air) without alteration, is unaffected by chlorine, and is very slowly acted upon by nitric acid.

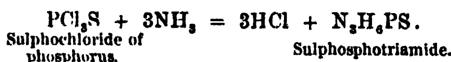
Action of ammonia on oxychloride of phosphorus.



$$PCl_3O \text{ (Oxychloride of phosphorus)} + 3NH_3 = 3HCl + N_3H_6PO \text{ (Phosphotriamide)}.$$

Of course the hydrochloric acid combines with the excess of ammonia to form hydrochlorate of ammonia, which may be washed out with water, leaving the phosphotriamide as a white insoluble solid, not easily attacked by acids or alkalies. It may be regarded as triphosphate of ammonia ($3(NH_4)_2O.P_2O_5$) *minus* six molecules of water, which would furnish two molecules of phosphotriamide.

If sulphochloride of phosphorus be submitted to the action of ammonia, sulphosphotriamide is obtained—



$$\underset{\text{Sulphochloride of phosphorus.}}{PCl_3S} + 3NH_3 = 3HCl + \underset{\text{Sulphosphotriamide.}}{N_3H_6PS}.$$

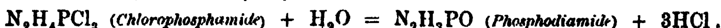
This compound may evidently be regarded as sulphophosphate of (sulphide of) ammonium ($3(NH_4)_2S.P_2S_5$) *minus* six molecules of hydrosulphuric acid.

Action of ammonia on pentachloride of phosphorus.



$$PCl_5 + 2NH_3 = 2HCl + N_2H_4PCl_3 \text{ (Chlorophosphamide)}.$$

The hydrochloric acid combines with the excess of ammonia, forming hydrochlorate of ammonia. By boiling chlorophosphamide with water, a very stable insoluble substance is obtained, known as *phosphodiamide*—



$$N_2H_4PCl_3 \text{ (Chlorophosphamide)} + H_2O = N_2H_3PO \text{ (Phosphodiamide)} + 3HCl.$$

This substance may be represented as derived from the phosphate of ammonia ($2(NH_4)_2O.H_2O.P_2O_5$) by the abstraction of six molecules of water, furnishing two molecules of phosphodiamide.

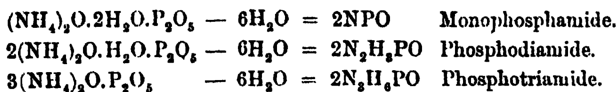
When phosphodiamide is heated it loses ammonia and becomes *monophosphamide*—



$$\underset{\text{Phosphodiamide.}}{N_2H_3PO} = NH_3 + \underset{\text{Monophosphamide.}}{NPO}.$$

which may be regarded as acid phosphate of ammonia ($(NH_4)_2O.2H_2O.P_2O_5$) *minus* six molecules of water, yielding two molecules of monophosphamide.

The phrase *amides of phosphoric acid* refers to those substances which may be represented as derived from the phosphates of ammonia by the loss of a certain number of molecules of water; thus—



$(NH_4)_2O.2H_2O.P_2O_5$	$- 6H_2O$	$= 2NPO$	Monophosphamide.
$2(NH_4)_2O.H_2O.P_2O_5$	$- 6H_2O$	$= 2N_2H_3PO$	Phosphodiamide.
$3(NH_4)_2O.P_2O_5$	$- 6H_2O$	$= 2N_3H_6PO$	Phosphotriamide.

All these substances yield ammonia and phosphate of potash when heated with hydrate of potash, when they acquire the elements of water.

ARSENIC.

As = 75 parts by weight.*

171. This element is often classed among the metals, because it has a metallic lustre and conducts electricity, but it is not capable of forming a base with oxygen, and the chemical character and composition of its compounds connect it in the closest manner with phosphorus.

* The specific gravity of the vapour of arsenic, like that of phosphorus, indicates that 75 parts by weight only occupy half a volume.

In its mode of occurrence in nature it more nearly resembles the sulphur group of elements, for it is occasionally found in the uncombined state (*native arsenic*), but far more abundantly in combination with various metals, forming *arsenides*, which frequently accompany the sulphides of the same metals. The following are some of the chief arsenides and *arsenio-sulphides* found in the mineral kingdom:—

Kupfernickel,	$NiAs$.
Arsenical nickel,	$NiAs_2$.
Tin-white cobalt,	$CoAs_2$.
Mispickel or arsenical pyrites,	$FeS_2.FeAs_2$.
Cobalt-glance,	$CoS_2.CoAs_2$.
Nickel-glance,	$NiS_2.NiAs_2$.

But arsenic also occurs, like the metals, in combination with sulphur, thus we have—

Red orpiment or realgar,	As_2S_2.
Yellow orpiment,	As_2S_3.

It is from these minerals that arsenic derives its name (ἀρσενικόν, *orpiment*), and the sulphides of arsenic being sulphur-acids, are found in combination with other sulphides; thus *red silver ore* is a compound of the sulphides of silver and arsenic ($3Ag_2S.As_2S_3$); *Tennantite* contains sulphide of arsenic combined with the sulphides of iron and copper; and *grey copper ore* is composed of sulphide of arsenic with the sulphides of copper, silver, zinc, iron, and antimony. In an oxidised form arsenic is found in *condurrite*, which contains arsenious acid (As_2O_3) and suboxide of copper. *Cobalt-bloom* consists of arseniate of cobalt ($3CoO.As_2O_5$).

Arsenical pyrites is one of the principal sources of arsenic and its compounds, though a considerable quantity is also obtained in the form of arsenious acid as a secondary product in the working of certain ores, especially those of copper, tin, cobalt, and nickel.

The substance used in the arts under the name of arsenic is really the oxide of arsenic or arsenious acid (As_2O_3); pure arsenic itself has very few useful applications, so that it is not the subject of an extensive manufacture. It can be extracted from arsenical pyrites ($FeS_2.FeAs_2$) by heating it in earthen cylinders fitted with iron receivers, in which the arsenic condenses as a metallic-looking crust, the heat expelling it from the pyrites in the form of vapour.

On a small scale it may be obtained by heating a mixture of arsenious acid with half its weight of recently calcined charcoal in a crucible (fig. 227), the mixture being covered with two or three inches of charcoal in very small fragments, and the crucible so placed that this charcoal may be heated to redness first, in order to ensure the reduction of any arsenious acid which might escape from below. In order to collect the arsenic, another crucible, having a small hole drilled through the bottom for the escape of gas, is cemented on to the first, in an inverted position, with fire-clay, and protected from the fire by an iron plate with a hole in it for the crucible. The reduction of arsenious acid by charcoal is thus represented—

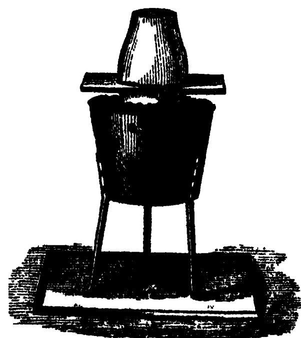


Fig. 227.—Extraction of arsenic.



$$As_2O_3 + C_3 = As_2 + 3CO.$$

For the sake of illustration, a small quantity of arsenic may be prepared from arsenious acid by a method commonly employed in testing for that substance. A small tube of German glass drawn out to a narrow point (A, fig. 228), and sealed with the aid of the blow-

pipe. A very minute quantity of arsenious acid is introduced into the point of the tube, and a few fragments of charcoal are placed in the tube itself at B. The charcoal is heated to redness with a blow-pipe flame, and the point is then heated so as to drive the arsenious acid in vapour over the red-hot charcoal, when a shining black ring of arsenic (C) will be deposited upon the cooler portion of the tube.

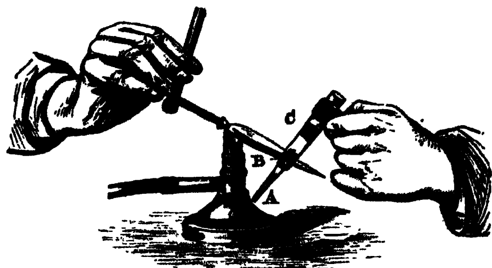


Fig. 228.—Reduction of arsenious acid.

The arsenic thus obtained is a brittle mass of a dark steel-grey colour and brilliant metallic lustre (sp. gr. 5·7). It does not fuse when heated, unless in a sealed tube, since it is converted into vapour at 356 F. It is not changed by exposure to air, unless powdered and moistened, when it is slowly converted into arsenious acid. When heated in air, it oxidises rapidly at about 160° F., giving off white fumes of arsenious acid and a characteristic garlic odour (recalling that of phosphorus). At a red heat it burns in air with a bluish white flame, and in oxygen with great brilliancy. It is not dissolved by water or any simple solvent (herein resembling the metals), but is oxidised and dissolved by nitric acid.

In its chemical relations to other elements, arsenic much resembles phosphorus, undergoing spontaneous combustion in chlorine, and easily combining with sulphur. Like phosphorus also, it combines with many metals, even with platinum, to form arsenides, and its presence often affects materially the properties of the useful metals. There are some reasons for believing in the existence of two allotropic forms of arsenic differing in chemical activity like those of phosphorus.

Pure arsenic does not produce symptoms of poisoning till a considerable period after its administration, being probably first oxidised in the stomach and intestines, and converted into arsenious acid.

Oxides of Arsenic.

172. Arsenic forms two well-defined acids with oxygen, corresponding to phosphorous and phosphoric acids.

	Formula.	By Weight.	
		Arsenic.	Oxygen.
Arsenious acid,	As_2O_3	150	48
Arsenic acid,	As_2O_5	150	80

Arsenious Acid (As_2O_3 = 198 parts by weight = 1 vol. = 1 vol. As + 3 vols. O)*.—Unlike phosphorus, arsenic, when burning in air, only combines with three atoms of oxygen. Arsenious acid, or *white arsenic*, is a very useful substance in many branches of industry. It is employed in the manufacture of glass, of several colouring-matters, and of shot. A large quantity is also consumed for the preparation of arsenic acid and

* The specific gravity of arsenious acid vapour is 198 times that of hydrogen, instead of 94 times, according to the usual law.

arseniate of soda; it is, indeed, the source from which nearly all the compounds of arsenic are procured. Small quantities of crystalline arsenious acid are occasionally found associated with the ores of nickel and cobalt.

Arsenious acid is manufactured by roasting the arsenical pyrites, chiefly obtained from the mines of Silesia, in *muffles* or ovens, through which air is allowed to pass, when the arsenic is converted into arsenious acid, and the sulphur into sulphurous acid, which are conducted into large chambers, in which the arsenious acid is deposited as a very fine powder. The iron of the pyrites is left partly as oxide, and partly as sulphate of iron. The removal of the arsenious acid from the condensing chambers is a very unwholesome operation, owing to its dusty and very poisonous character. The workmen are cased in leather, and protect their mouths and noses with damp cloths, so as to avoid inhaling the fine powder.

This rough arsenious acid is subjected to a second sublimation on a smaller scale in iron vessels, when it is obtained in the form of a semi-transparent glassy mass known as *vitreous arsenious acid*, which gradually becomes opaque when kept, and ultimately resembles porcelain. The white arsenic sold in the shops is a fine powder, dangerously resembling flour in appearance, but so much heavier (sp. gr. 3·7) that it ought not to be mistaken for it. When examined under the microscope, it appears in the form of irregular glassy fragments, mixed with octahedral crystals. Arsenious acid softens when gently heated, but does not fuse (unless in a sealed tube), being converted into vapour at 380° F., and depositing in brilliant octahedral crystals upon a cool surface. The experiment may be made in a small tube sealed at one end, the upper part of which should be slightly warmed before heating the arsenious acid, so as to prevent too rapid condensation, which is unfavourable to the formation of distinct crystals.* The octahedra are best examined with a binocular microscope. This common poison may fortunately be still more easily recognised by sprinkling it upon a red-hot coal, when a strong odour of garlic is perceptible, due to the reduction of the acid by the heated carbon; the vapour of arsenious acid itself is inodorous. The sparing solubility of arsenious acid in water is very unfavourable to its action as a poison, for, when thrown into ordinary liquids, it is dissolved in very small quantity, the greater part of it collecting at the bottom. Even when arsenious acid is taken into the stomach in a solid state, its want of solubility delays its passage into the blood sufficiently to give a better chance of antidotal treatment than in the case of most other common poisons. Its comparative insolubility is shown by its being almost tasteless.

When thrown into water, arsenious acid exhibits great repulsion for the particles of that liquid, and collects in a characteristic manner round little bubbles of air, forming small white globes which are not wetted by the water. Even if the acid be stirred with the water, and allowed to remain in contact with it for some hours, a pint of water (20 oz.) would not take up more than 20 grs. of arsenious acid. The smallest dose which has been known to prove fatal is 2·5 grs. If boiling water be poured upon powdered arsenious acid, and allowed to remain in contact with it till cold, it will dissolve about $\frac{1}{100}$ of its weight (22 grs. in a pint).

When powdered arsenious acid is boiled with water for two or three

* When arsenious acid is fused in a long tube, sealed at both ends, and buried in hot sand, the mass, after cooling, is found to contain some prismatic crystals, which are also sublimed on those parts of the tube which have been heated above 390° F.

hours, 100 parts by weight of water may be made to dissolve 11·5 parts of the acid, and when the solution is allowed to cool, about 9 parts of the acid will be deposited in octahedral crystals, leaving 2·5 parts dissolved in 100 of water (219 grs. in a pint).

This great increase in the solubility of the arsenious acid by long boiling with water, is usually attributed to the conversion of the opaque or crystalline variety of the acid, which always composes the powder, into the vitreous modification, which is the more soluble in water. Water, heated with arsenious acid in a sealed tube, may be made to dissolve its own weight of the acid; as the solution cools, it first deposits prismatic crystals, and afterwards the ordinary octahedral form. The solution of arsenious acid is very feebly acid to blue litmus paper.

Arsenious acid dissolves abundantly in hot hydrochloric acid (a part of it being converted into terchloride of arsenic), and as the solution cools, part of the acid is deposited in large octahedral crystals. It is said that if the vitreous acid be dissolved in hydrochloric acid, the formation of these crystals will be attended by flashes of light, visible in a darkened room; but the opaque variety does not exhibit this phenomenon.

The vitreous arsenious acid has a slightly higher specific gravity than the opaque form, and fuses rather more easily. The opaque variety appears to be identical in its properties with crystallised arsenious acid.

Solutions of the alkalies readily dissolve arsenious acid, forming alkaline arsenites, the solutions of which are capable of dissolving arsenious acid more easily than water, and deposit it in crystals on cooling. Arsenious acid is sometimes deposited in *prismatic* crystals from its solution in potash, and the same form of crystallised arsenious acid has been found native. On adding a small quantity of hydrochloric acid to the solution of the alkaline arsenite, a white precipitate of arsenious acid is formed.

Arsenious acid has the property of preventing the putrefaction of skin and similar substances, and is occasionally employed for the preservation of objects of natural history, &c.

Arsenites.—Arsenious acid does not destroy the alkaline reaction of the alkalies, and it does not decompose the alkaline carbonates unless heat is applied, proving it to be a feeble acid. The arsenite of ammonia is very unstable, evolving ammonia freely when exposed to the air. When arsenious acid is dissolved in a hot solution of ammonia, octahedral crystals of the acid are deposited on cooling, notwithstanding the presence of ammonia in large excess.

When the carbonates of potash and soda are fused with an excess of arsenious acid, brilliant transparent glasses are obtained which are similar in composition to glass of borax ($K_2O.2As_2O_3$ and $Na_2O.2As_2O_3$).

If an alkaline arsenite be fused in contact with platinum, the latter is easily melted, combining with a small proportion of arsenic to form a fusible arsenide of platinum, a portion of the arsenious acid being converted into arsenic acid; $5As_2O_3 = 3As_2O_5 + As_4$. The alkaline arseniates are so much more stable than the arsenites, that the latter exhibit a great tendency to pass into the former, with separation of arsenic.

In consequence of the feeble acid character of arsenious acid, and the want of stability of the alkaline arsenites, there is some difficulty in ascertaining whether it is a monobasic acid or otherwise. The arsenite of silver ($3Ag_2O.As_2O_3$), however, contains 3 molecules of oxide of silver combined with 198 parts of arsenious acid; and arsenite of zinc ($3ZnO.As_2O_3$) contains 3 molecules of oxide of zinc combined with 198

parts of arsenious acid. Moreover, the arsenite of magnesia, dried at 400° F., has the composition $2MgO.H_2O.As_2O_3$, so that arsenious acid would appear to resemble boracic acid, in requiring 3 molecules of potash or soda to form a completely saturated compound. No compound of the anhydrous acid with water or its elements has yet been obtained.

The arsenites of potash and soda in solution are sometimes employed as sheep-dipping compositions; and an arsenical soap, composed of arsenite of potash, soap, and camphor, is used by naturalists to preserve the skins of animals. Arsenite of soda is also occasionally employed for preventing incrustations in steam-boilers, being prepared for that purpose by dissolving 2 molecules of arsenious acid in 1 molecule of carbonate of soda.

Scheele's green is an arsenite of copper ($2CuO.H_2O.As_2O_3$) prepared by dissolving arsenious acid in a solution of carbonate of potash, and decomposing the arsenite of potash thus produced by adding sulphate of copper, when the arsenite of copper is precipitated. This poisonous colour is used to impart a bright green tint to paper hangings, and is sometimes injurious to the health of the occupants of rooms thus decorated, since the arsenite of copper is often easily rubbed off the paper, and diffused through the air in the form of a fine dust, a small portion of which is inhaled with every breath.

The presence of the arsenite of copper in a sample of such paper is readily proved by soaking it in a little ammonia, which will dissolve the arsenite of copper to a blue liquid, the presence of arsenic in which may be shown by acidifying it with a little pure hydrochloric acid, and boiling with one or two strips of pure copper, which will become covered with a steel-grey coating of arsenide of copper. On washing the copper, drying it on filter-paper, and heating it in a small tube (fig. 229), the arsenic will be converted into arsenious acid, which will deposit in brilliant octahedral crystals on the cool part of the tube. It is obvious that, to avoid mistakes, the ammonia, hydrochloric acid, and copper should be examined in precisely the same way, without the suspected paper, so as to render it certain that the arsenic is not derived from them.

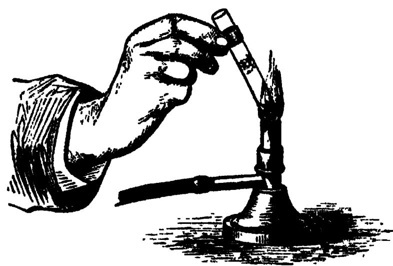


Fig. 229.

The effective green colour of the arsenite of copper also leads to its employment as a colour for feathers, muslin, &c., where it is very injurious to the health of the work-people. It has even been ignorantly or recklessly used for colouring twelfth-cake ornaments, &c.

In quantities short of poisonous doses, arsenious acid appears to have a remarkable effect upon the animal body. Grooms occasionally employ it to improve the appearance of horses, and in Styria it seems to be taken by men and women for the same purpose, apparently favouring the secretion of fat. It is said that a continuance of the custom developes a craving for this drug, and enables large doses to be taken without immediate danger, though the ultimate consequences are very serious.

Solution of arsenite of potash (*Fowler's solution*) has long been used in medicine.

173. *Arsenic acid* ($As_2O_5 = 230$ parts by weight).—This acid has acquired great importance in the chemical arts during the last few years, having been employed to replace the expensive tartaric acid used in

calico-printing, and to furnish, by its action upon aniline, the magnificent dye known as *Magenta*.

Arsenic acid is prepared by oxidising arsenious acid with three-fourths of its weight of nitric acid of sp. gr. 1·35, when it dissolves with evolution of much heat and abundant red fumes of nitrous acid—



$$As_2O_3 + H_2O.N_2O_5 + 2H_2O = N_2O_3 + 3H_2O.As_2O_5.$$

After cooling, the solution deposits very deliquescent prismatic crystals containing $3H_2O.As_2O_5.Aq$. When these are heated to 212° F. they melt, and the liquid gradually deposits needle-like crystals of trihydrated arsenic acid, $3H_2O.As_2O_5$, corresponding to common or tribasic phosphoric acid. At 300° F. the hydrate $2H_2O.As_2O_5$ may be obtained, and at a temperature of 500° F. a white mass of anhydrous arsenic acid (As_2O_5) is left. If this be heated to redness, it fuses and is decomposed into arsenious acid and oxygen.

The hydrates of arsenic acid have acquired unusual importance, in consequence of a costly trial, in the law courts, of the question, whether the patent for Magenta dye could be pronounced invalid because the patentee had described it as being producible by the action of *dry* arsenic acid upon aniline; whereas the *anhydrous* acid, acting upon aniline, will not furnish the colour, though either of the solid (and therefore *dry* in popular language) hydrates will do so. The patent was eventually invalidated, though not merely upon this question.

Anhydrous arsenic acid has very much less attraction for water than the anhydrous phosphoric acid to which it corresponds; it deliquesces slowly in air, and dissolves rather reluctantly in water. Neither does it appear that its combinations with water differ from each other, like the phosphoric acids, in the salts to which they give rise, arsenic acid forming tribasic salts only, like common phosphoric acid. The arseniates correspond very closely to the tribasic phosphates with which they are isomorphous (*i.e.*, identical in crystalline form). Thus the three arseniates of soda are similar in composition to the three tribasic phosphates of soda, their formulæ being $3Na_2O.As_2O_5.24Aq.$; $2Na_2O.H_2O.As_2O_5.24Aq.$; and $Na_2O.2H_2O.As_2O_5.Aq$. But if the two last salts be heated, they lose their basic water without giving rise to new salts corresponding to the pyrophosphate and metaphosphate of soda, and resume their former condition when placed in contact with water.

The common arseniate of soda ($2Na_2O.H_2O.As_2O_5.14Aq.$) is largely used by calico printers as a substitute for the dung-baths formerly employed, since, like the common phosphate of soda, it possesses the feebly alkaline properties required in that particular part of the process. It is manufactured by combining arsenious acid with soda, and heating the resulting arsenite of soda with nitrate of soda, from which it acquires oxygen, becoming converted into arseniate of soda.

Arsenic acid is a much more powerful acid than arsenious acid, being comparable, in this respect, with phosphoric acid. It appears to be less poisonous than arsenious acid.

174. *Arsenietted hydrogen* (AsH_3 = 78 parts by weight = 2 vols. = ½ vol. As + 3 vols. H).—The only compound of arsenic and hydrogen, the existence of which has been satisfactorily established, is that which corresponds to ammonia and phosphuretted hydrogen gas, and is represented by the formula, AsH_3. It is prepared by the action of sulphuric

acid diluted with three parts of water upon the arsenide of zinc, obtained by heating equal weights of zinc and arsenic in an earthen retort; $Zn_3As_2 + 3(H_2O.SO_3) = 2AsH_3 + 3(ZnO.SO_3)$. The gas is so poisonous in its character that its preparation in the pure state is attended with danger. It has a sickly alliaceous odour, and may be liquefied at $-40°$ F. It is inflammable, burning with a peculiar livid flame, producing water and fumes of arsenious acid; $2AsH_3 + O_6 = As_2O_3 + 3H_2O$. The chief interest attaching to this gas depends upon the circumstance that its production allows of the detection of very minute quantities of arsenic in cases of poisoning.

The application of this test, known as Marsh's test, is the safest method of preparing arsenietted hydrogen in order to study its properties, for it is obtained so largely diluted with free hydrogen that it ceases to be so very dangerous. Some fragments of granulated zinc are introduced into a half-pint bottle (fig. 230), provided with a funnel-tube (A), and a narrow tube (B) bent at right angles and drawn out to a jet at the extremity; this tube should be made of German glass, so that it may not fuse easily. The bottle having been about one-third filled with water, a little diluted sulphuric acid is poured down the funnel-tube so as to cause a moderate evolution of hydrogen, and after about five minutes (to allow the escape of the air) the hydrogen is kindled at the jet. If a few drops of a solution obtained by boiling arsenious acid with water be now poured down the funnel, arsenietted hydrogen will be evolved together with the hydrogen—

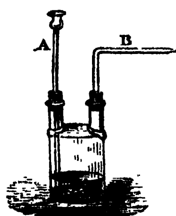
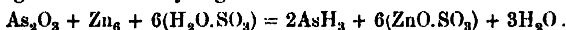
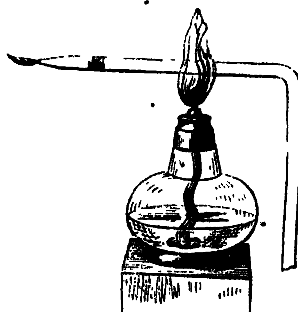


Fig. 230.


$$As_2O_3 + Zn_6 + 6(H_2O.SO_3) = 2AsH_3 + 6(ZnO.SO_3) + 3H_2O.$$

The hydrogen flame will now acquire the livid hue above referred to, and a white smoke of arsenious acid will rise from it. If a piece of glass or porcelain be depressed upon the flame (fig. 231), it will acquire a metallic-looking coating of arsenic, just as carbon would be deposited from an ordinary gas-flame. Arseniètted hydrogen is easily decomposed by heat, so that if the glass tube through which it passes be heated with a spirit-lamp (fig. 232), a dark *mirror* of arsenic will be deposited a little in front of the heated part, and the flame of the gas will lose its livid hue. These deposits of arsenic are extremely thin, so that a very minute quantity of arsenic is required to form them, thus rendering the test one of extraordinary delicacy. It must be remembered, however, that both sulphuric acid and zinc are liable to contain arsenic, so that erroneous results may be very easily arrived at by this test in the hands of any but those specially devoted to such investigations.


Fig. 231.


Fig. 232.

Arseniètted hydrogen, like sulphuretted hydrogen, causes dark precipitates in many metallic solutions.

Phosphuretted hydrogen, arseniètted hydrogen, and ammonia, constitute a group of hydrogen compounds having certain properties in common, which distinguish them from the compounds of hydrogen with other elements.

Two volumes of each of these gases contain three volumes of hydrogen.

They are all possessed of peculiar odours, that of ammonia being the most powerful, and that of arseniètted hydrogen the least.

Ammonia is powerfully alkaline, phosphuretted hydrogen exhibits some tendency to play an alkaline part, whilst arseniètted hydrogen seems devoid of alkaline disposition.

All these are inflammable, ammonia being the least so of the group; and all are decomposed by heat, ammonia least easily, and arsenietted hydrogen most easily.

They are all producible from their corresponding oxygen compounds, viz., N_2O_3, P_2O_3, and As_2O_3, by the action of nascent hydrogen (*e.g.*, by contact with zinc and diluted sulphuric acid).

All three are the prototypes of various organic bases which contain some compound radical in place of the hydrogen, thus—

NH_3	is the prototype of	triethylamine,	$N(C_2H_5)_3$
PH_3	,, ,,	triethylphosphine,	$P(C_2H_5)_3$
AsH_3	,, ,,	triethylarsine,	$As(C_2H_5)_3$.

175 *Terchloride of arsenic.*—Only one compound of chlorine with arsenic ($AsCl_3$) has yet been obtained; the chloride corresponding to pentachloride of phosphorus remains to be discovered.* The terchloride may be formed by the direct union of its elements, but the simplest laboratory process for procuring it consists in heating arsenious acid in dry chlorine gas, in a tubulated retort (A, fig. 233). extemporised from a Florence flask (see p. 103). The arsenious acid soon melts, and the terchloride of arsenic distils over, leaving a melted mass in the flask, which forms a brilliantly transparent glass on cooling, the composition of which varies somewhat with the temperature employed, but appears to be essentially $2As_2O_3.As_2O_5$. The same vitreous compound may be obtained by fusing arsenious and arsenic acids together. The formation of the terchloride of arsenic may be represented by the equation, $11As_2O_3 + Cl_{12} = 4AsCl_3 + 3(2As_2O_3.As_2O_5)$.

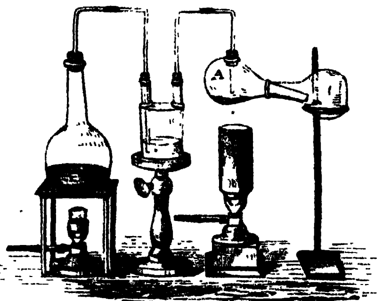


Fig. 233.

Terchloride of arsenic bears a great general resemblance to terchloride of phosphorus; it is a heavy (sp. gr. 2·2), pungent, fuming liquid, decomposed by the moisture of the air, its vapours depositing a white coating of arsenious acid upon the objects in its immediate neighbourhood. When poured into water it deposits arsenious acid; $2AsCl_3 + 3H_2O = As_2O_3 + 6HCl$; but when dissolved in the smallest possible quantity of water, it deposits crystals of the formula $AsOCl.H_2O$.

When arsenious acid is dissolved in hydrochloric acid, terchloride of arsenic is formed, $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$, and remains undecomposed by the water in the presence of strong hydrochloric acid, but if water be added, arsenious acid is precipitated. When the solution of arsenious acid in hydrochloric acid is distilled, the terchloride of arsenic distils over, and this is sometimes a convenient method of separating arsenic from articles of food, &c., in testing for that poison. When heated in dry hydrochloric acid gas, arsenious acid yields a glassy compound, which contains $As_2O_3.AsClO$; $3As_2O_3 + 2HCl = 2(As_2O_3.AsClO) + H_2O$.

In composition by volume, the terchloride of arsenic resembles terchloride of phosphorus, containing ½ vol. of arsenic vapour, and 3 vols. of chlorine condensed into 2 vols., the specific gravity of its vapour being 6·3.

Terbromide of arsenic much resembles the terchloride in its chemical characters, but is a solid crystalline substance, easily fusible.

176. *Teriodide of arsenic* (AsI_3) is remarkable for not being decomposed by water, like the corresponding phosphorus compound. When obtained by heating arsenic and iodine together, it sublimes in brick-red flakes, which, if prepared on a large scale, hang in long laminæ like sea-weed. It may be dissolved in boiling water, and crystallises out unchanged. It may even be prepared by heating 3 parts of arsenic

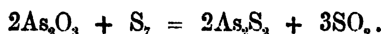
* Nicklès appears to have succeeded in forming the pentachloride by the action of hydrochloric acid gas on arsenic acid in presence of ether; he describes it as very unstable, and easily converted into the terchloride.

with 10 of iodine and 100 of water, when the solution deposits red crystals of the hydrated teriodide, from which the water may be expelled by a gentle heat.

The *terfluoride of arsenic* (AsF_3) resembles the terchloride, but is much more volatile. It may be obtained by distilling 4 parts of arsenious acid with 5 of fluor-spar and 10 of strong sulphuric acid in a leaden retort (see p. 181). It does not attack glass unless water be present, which decomposes it into arsenious and hydrofluoric acids.

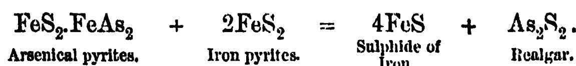
177. SULPHIDES OF ARSENIC.—There are three well-known sulphides of arsenic, having the composition As_2S_2, As_2S_3, and As_2S_5, the two former being found in nature.

Realgar (As_2S_2) is a beautiful mineral, crystallised in orange-red prisms; but the *red orpiment* used in the arts is generally prepared by heating a mixture of arsenious acid and sulphur, when sulphurous acid escapes, and an orange-coloured mass of realgar is left—



$$2As_2O_3 + S_7 = 2As_2S_2 + 3SO_2.$$

Another process for preparing it consists in distilling arsenical pyrites with sulphur or with iron pyrites—

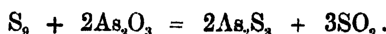


$$\underset{\text{Arsenical pyrites.}}{FeS_2.FeAs_2} + \underset{\text{Iron pyrites.}}{2FeS_2} = \underset{\text{Sulphide of Iron.}}{4FeS} + \underset{\text{Realgar.}}{As_2S_2}.$$

The realgar distils over, and condenses to a red transparent solid. Realgar burns in air with a blue flame, yielding arsenious acid and sulphurous acid. If it be thrown into melted saltpetre, it burns with a brilliant white flame, being converted into arseniate and sulphate of potash. This brilliant flame renders realgar an important ingredient in *Indian fire* and similar compositions for fire-works and signal lights. A mixture of one part of red orpiment with 3·5 parts of sublimed sulphur and 14 parts of nitre is used for signal-light composition.

Realgar is not easily attacked by acids; nitric acid, however, dissolves it, with the aid of heat, forming arsenic acid and sulphuric acid, with separation of part of the sulphur in the free state. Alkalies (potash, for example) partly dissolve it, leaving a brown substance, which appears to be a subsulphide of arsenic ($As_{12}S$).

Yellow orpiment, or *tersulphide of arsenic* (As_2S_3), is found native in yellow prismatic crystals. The paint known as *King's yellow* is a mixture of tersulphide of arsenic and arsenious acid, prepared by subliming a mixture of sulphur with arsenious acid—



$$S_9 + 2As_2O_3 = 2As_2S_3 + 3SO_2.$$

It is, of course, very poisonous.

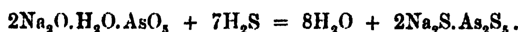
This substance, like realgar, is not much affected by acids, excepting nitric acid; but it dissolves entirely in potash, forming arsenite of potash and *sulpharsenite* of (sulphide of) potassium; $12KHO + 2As_2S_3 = 3K_2S.As_2S_3 + 3K_2O.As_2O_3 + 6H_2O$. Ammonia also dissolves it easily, forming a colourless solution which is employed for dyeing yellow, since if a piece of stuff be dipped into it and exposed to air, the ammonia will volatilise, leaving the yellow orpiment behind.

The formation of the characteristic yellow tersulphide is turned to account in testing for arsenic; if a solution prepared by boiling arsenious acid with distilled water be mixed with a solution of hydrosulphuric acid, a bright yellow liquid is produced, which looks opaque by reflected, but transparent by transmitted light, and may be passed through a filter without leaving any solid matter behind. This solution probably contains a soluble compound of tersulphide of arsenic with hydrosulphuric acid ($3H_2S.As_2S_3$); it is, however, very unstable, being decomposed by evaporation, with precipitation of the tersulphide. The addition of a little hydrochloric acid, or of sal-ammoniac, and many other neutral salts, will also cause a separation of the ter-

sulphide from this solution; even the addition of a hard water will have that effect. If the solution of arsenious acid be acidified with hydrochloric acid before adding the hydrosulphuric acid, the bright yellow tersulphide of arsenic is precipitated at once, and may be distinguished from any other similar precipitate by its ready solubility in solution of carbonate of ammonia.

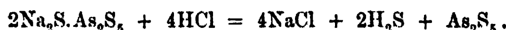
From its combining readily with the alkaline sulphides to form soluble compounds, the tersulphide of arsenic is often called *sulpharsenious acid.*

Pentasulphide of arsenic (As_2S_5), or *sulpharsenic acid,* possesses far less practical importance than the preceding sulphides; it may be obtained by fusing the tersulphide with sulphur, when it forms an orange-coloured glass, easily fusible, and capable of being sublimed without change. When hydrosulphuric acid gas is passed through solution of arsenic acid, a white precipitate of sulphur is first obtained, the hydrogen reducing the arsenic acid to arsenious acid; $As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + S_2$; and if the passage of the gas be continued, the arsenious acid is decomposed, and tersulphide of arsenic is precipitated; these changes are much accelerated by heat. But if a solution of arseniate of soda be saturated with hydrosulphuric acid, it is converted into sulpharseniate of (sulphide of) sodium—



$$2Na_2O.H_2O.AsO_5 + 7H_2S = 8H_2O + 2Na_2S.As_2S_5.$$

On adding hydrochloric acid to this solution, a bright yellow precipitate of pentasulphide of arsenic is obtained—



$$2Na_2S.As_2S_5 + 4HCl = 4NaCl + 2H_2S + As_2S_5.$$

Pentasulphide of arsenic is one of the most powerful of the sulphur acids; it expels hydrosulphuric acid from its combinations with the alkaline sulphides, and is capable of forming, with these, sulpho-salts, containing respectively one, two, and three molecules of the alkaline sulphide, which may be obtained by the action of hydrosulphuric acid upon the corresponding arseniates.

GENERAL REVIEW OF THE NON-METALLIC ELEMENTS.

178. At the conclusion of the history of the non-metals, it may be well to call attention to the points of resemblance which classify them into separate groups or families, most of which are connected, by some analogies, with one or more members of the class of metals.

Hydrogen stands alone among the non-metals, its chemical properties and functions being widely different from those of any other non-metal, but connecting it very closely with the most highly electropositive (or *basylous*) metals, such as potassium and sodium.

Oxygen, Sulphur, Selenium, and *Tellurium* compose a group, the members of which (in the state of vapour) combine with twice their volume of hydrogen to form compounds which (in the state of vapour) occupy the same volume as the hydrogen occupied before combination. All these hydrogen compounds are capable of playing a feebly acid part, and their hydrogen may be displaced by an equivalent weight of a metal to produce compounds exhibiting a general agreement in chemical properties. This group is connected with the metals through tellurium, not only by its physical properties, but by its forming an oxide (TeO_2), which occasionally acts as a weak base.

Nitrogen, Phosphorus, and *Arsenic* are connected together by the general analogy of their hydrogen and oxygen compounds, the two last members of the group being far more closely connected with each other than with nitrogen. With the metals, they are connected through arsenic, the hydrogen compound of which is very similar in properties, and probably in composition, to antimonietted hydrogen; arsenious acid (As_2O_3) is also capable of occupying the place of teroxide of antimony (Sb_2O_3) in certain salts of that oxide; and the sulphides of antimony correspond in composi-

tion, and in some of their properties, to those of arsenic. One form of arsenious acid (the prismatic) is isomorphous with native oxide of antimony, and this oxide may be obtained in octahedra, the ordinary form of arsenious acid, so that these oxides are *isodimorphous.*

These elements are also connected with the oxygen group through sulphur, selenium, and tellurium, the relations of which to hydrogen and the metals are somewhat similar to those of phosphorus and arsenic.

Carbon, Boron, and *Silicon* resemble each other in their allotropic forms, their resistance to fusion and volatilisation, and their forming feeble acids with oxygen. To the metals they are allied through silicon, which resembles tin in the composition and character of its oxide and chloride.

This group is connected with the nitrogen group through boron, for boracic acid resembles arsenious acid in its relations to bases, and in forming vitreous compounds with the alkalies. In certain compounds boracic and arsenious acids are interchangeable.

Chlorine, Bromine, Iodine, and *Fluorine* are intimately connected by numerous analogies, which have been already pointed out (p. 186). Some of the properties of iodine, as its relations to oxygen, and the solubility of its terchloride in water, connect it slightly with the metals, whilst the general correspondence in composition between the chlorides and the oxides, allies this group to the oxygen group of non-metallic elements.

If the non-metals be classified according to their quantivalence (see p. 158), it will be found that, with only few exceptions, the classification will coincide with that founded upon their chemical analogies in other respects. Thus, the members of the oxygen group are all diatomic, or capable of combining with two atoms of hydrogen, as shown by the formulæ of their hydrogen compounds, H_2O, H_2S, H_2Se, H_2Te. The nitrogen group is generally represented as triatomic, (though, from our present knowledge of the vapour densities of phosphorus and arsenic, these elements are strictly hexatomic,) their hydrogen compounds being NH_3, PH_3, and AsH_3. Boron is also a triatomic element, for, in BCl_3, the boron occupies the place of three atoms of hydrogen.

Carbon and silicon, however, are tetratomic elements, as shown in marsh-gas, CH_4, and in chloride of silicon, $SiCl_4$.

Chlorine, bromine, iodine, and fluorine are monatomic, their hydrogen compounds having the formulæ, HCl, HBr, HI, and HF.

The atomicity or quantivalence of an element is sometimes expressed in a formula by a dash, or dashes, placed above and to the right of the element; thus the symbols, Cl', O'', N''', C'''', indicate the respective atomicities of those elements. When the atomicity of an element is taken into account, it helps to explain the constitution of compounds which would otherwise appear quite anomalous. For example, there is a compound of the molecular formula, N_3H_6P, obtained by the action of terchloride of phosphorus upon ammonia; recollecting the triatomic character of phosphorus, we perceive this compound to represent three molecules of ammonia (N_3H_9), in which phosphorus is the substitute for three atoms of hydrogen, which is at once expressed if the formula be written, N_3H_6P'''. Again, chlorocarbonic acid, $COCl_2$, appears an inexplicable association of elements, until the tetratomic character of carbon and diatomic character of oxygen are taken into account, as in the formula $C''''O''Cl'_2$ when it appears that the diatomic oxygen and the two atoms of monatomic chlorine are the substitutes for four atoms of hydrogen

in marsh-gas, CH_4, and it might plausibly be given as a reason why the apparently indifferent carbonic oxide should combine with chlorine, that the atomicity of the carbon is only partly satisfied in carbonic oxide, which contains only oxygen equal in value to two atoms of hydrogen, the tetratomic carbon requiring the value of two more atoms of hydrogen to complete the compound atom. In carbonic acid, $C''''O''_2$, the two atoms of diatomic oxygen fully complete the compound.

In a similar manner the absorption of carbonic oxide by subchloride of copper may be explained; for the atomic formula of that salt is $Cu'Cl'$, and hence it is capable of supplying the two absent atoms in $C''''O''$.

Many more examples of the same kind might be gathered from the preceding pages, but these will probably be sufficient to mark the importance of remembering the atomicities of the elements in speculative chemistry; indeed, without this clue it is impossible to find any meaning whatever in a very large number of the formulæ of organic substances, whilst with it, not only their constitution, but in many cases their mode of formation, becomes as intelligible as that of the simplest mineral compounds.

CONSTITUTION OF SALTS.

179. The term *salt*, like *acid* and *alkali*, was, of course, purely empirical in its origin, being conferred upon every solid substance which exhibited any of the prominent characters of sea-salt (sal, *brine*, σάλος, *the sea*), such as solubility in water and tendency to crystallisation.

When the great mass of chemical facts accumulated by the alchemists, metallurgists, and apothecaries, came to be classified, and the distinction between acids and bases was recognised, the term salt was extended to all those substances, such as *muriate of soda*, nitrate of potash, carbonate of lime, &c., from which a base and an acid could be obtained, without regard to their solubility or tendency to crystallise. When the analytical powers of the chemist were more fully developed, it was found that muriate of soda and a large class of similar salts did not contain an acid and a base, but that these substances were *produced* and not *educed* from the salts by the chemical operations to which they were subjected. Thus muriate of soda, from which muriatic acid had been so easily *produced* by the action of sulphuric acid, was shown to contain only sodium and chlorine.

This led to a classification of salts into *haloid* salts (ἅλς, *the sea*), or those composed, like chloride of sodium, of a metal combined with a salt-radical or halogen, and *oxy-acid* salts, or those composed of a metallic oxide combined with an oxygen acid. (It will have been remarked that the tendency of modern chemistry is to represent this second class of salts by formulæ which do not admit the existence of the metal as an oxide in the salt.)

Independently of all differences of opinion with respect to the actual constitution of salts, the criterion by which the claims of a substance to this title can be estimated is this: *a salt is a compound which may be formed by the action of an acid upon a base*, water, which is a very general result of such action, being excepted.

The oxy-acid salts soon came to be divided into *neutral* and *acid* salts, according to their effect upon vegetable colours and the organ of taste,

and a class of *basic* salts was afterwards added, when it was found that a neutral soluble salt sometimes became insoluble by combining with an additional quantity of base.

Further investigation has shown that the neutral taste of a salt, and its neutrality to test-papers, depend less upon the proportions of the acid and base which are contained in it, than upon the chemical energy of these substances.

Thus, *potash* combined with one molecule of *sulphuric acid* forms a salt which is perfectly neutral to taste and to litmus-papers, whilst with one molecule of *carbonic acid* it forms a strongly alkaline salt; and one molecule of *sulphuric acid* combined with one molecule of *oxide of zinc* forms a salt which is strongly acid to test-papers.

A salt may, therefore, be neutral in chemical constitution, and acid or alkaline in reaction to test-papers, and it has been proposed to employ the term *normal* to designate those salts which are neutral in chemical constitution, and to restrict the term *neutral* to those salts which are neither acid nor alkaline to test-papers. Thus, sulphate of potash would be both a neutral and a normal salt, whilst sulphate of zinc and carbonate of potash are normal, but not neutral salts.

A *normal salt* is one in which the oxygen contained in the base bears a certain proportion to the oxygen contained in the acid, this proportion being fixed for each acid.

Thus, a normal carbonate is one in which the oxygen of the base bears to the oxygen of the acid the ratio of 1 : 2, as in normal carbonate of potash, $K_2O.CO_2$.

A normal sulphate is one in which the oxygen of the base bears to the oxygen of the acid the ratio of 1 : 3, as in normal sulphate of zinc $ZnO.SO_3$.

To form a normal salt with a sesquioxide, 3 molecules of sulphuric acid are required. Thus the sulphate of alumina, $Al_2O_3.3SO_3$, although powerfully acid to test-papers, is a normal sulphate, for the oxygen of the base bears to the oxygen of the acid the ratio of 1 : 3.

An *acid salt* is one in which the oxygen in the acid is in greater proportion than in the normal ratio. Thus bicarbonate of potash, $K_2O.H_2O.2CO_2$, is acid in chemical constitution, though alkaline to test-papers, for the oxygen of the base is to the oxygen of the acid as 1 : 4, whilst the normal ratio for carbonates is 1 : 2. Acid salts usually have the deficiency of base supplied by water, but not invariably, as in fused borax, $Na_2O.2BO_3$, bichromate of potash $K_2O.2CrO_3$, dried bisulphate of soda, $Na_2O.2SO_3$.

A *basic salt* is one in which the oxygen in the base is in greater proportion than in the normal ratio. Thus, white lead, $2(PbO.CO_2)$, $PbO.H_2O$, is a basic carbonate, for the oxygen of the base is to the oxygen of the acid as 3 : 4, whereas the normal ratio is 2 : 4 or 1 : 2.

Aluminite, $Al_2O_3.SO_3.9H_2O$, is a basic salt, for the oxygen in the base is to the oxygen in the acid as 3 : 3, whilst the normal ratio is 1 : 3.

In order to explain the results obtained by the actual analysis of salts, it may be supposed that the salts are formed upon the type of the hydrated acid, and that a normal salt is one in which the water in the hydrated acid is displaced by an equivalent quantity of base; thus the sulphates are formed upon the type of oil of vitriol, $H_2O.SO_3$, and the H_2O must be displaced by K_2O to form the normal sulphate of potash; but when alumina (Al_2O_3) is employed to displace the water, one-third of the quantity represented by that formula would be equivalent to the H_2O (for

Al_2 is equivalent to H_6), and therefore the normal sulphate of alumina would be $\frac{1}{3}$ $(Al_2O_3).SO_3$, or avoiding the fraction, $Al_2O_3.3SO_3$.

The following are the normal ratios for some of the most important classes of salts :—

Salts.	Normal Ratio.	Examples.	
Carbonates,	1 : 2	$Na_2O.CO_2$.	Carbonate of soda.
Borates,	3 : 3 ?	$3MgO.B_2O_3$	Borate of magnesia.
Silicates,	2 : 2	$2FeO.SiO_2$	Forge cinder.
Nitrates,	1 : 5	$K_2O.N_2O_5$	Saltpetre.
Chlorates,	1 : 5	$K_2O.Cl_2O_5$	Chlorate of potash.
Sulphites,	1 : 2	$Na_2O.SO_2$	Sulphite of soda.
Sulphates,	1 : 3	$CaO.SO_3$	Sulphate of lime.
Metaphosphates,	1 : 5	$Na_2O.P_2O_5$	Metaphosphate of soda.
Pyrophosphates,	2 : 5	$2Na_2O.P_2O_5$	Pyrophosphate of soda.
Orthophosphates,	3 : 5	$3CaO.P_2O_5$	Bone phosphate of lime.
Arsenites,	3 : 3 ?	$3Ag_2O.As_2O_3$	Arsenite of silver.
Arseniates,	3 : 5	$3CoO.As_2O_5$	Cobalt bloom.
Chromates,	1 : 3	$K_2O.CrO_3$	Chromate of potash.
Permanganates,	1 : 7	$K_2O.Mn_2O_7$	Permanganate of potash.

Binary theory of the constitution of salts.—The circumstance that it is only the hydrogen of the hydrated acid that is displaced by the metal, has given rise to the *binary theory* of salts, according to which all acids and salts are constituted after the type of hydrochloric acid and chloride of sodium; the acid being composed of hydrogen combined with a *compound salt-radical* made up of the other elements present in the acid. Thus, sulphuric acid $(H_2O.SO_3)$ would become H_2,SO_4 nitric acid, H,NO_3; metaphosphoric acid, H,PO_3; pyrophosphoric, H_4,P_2O_7; tribasic phosphoric, H_3,PO_4, and their normal salts are formed by the substitution of an equivalent quantity of a metal for the hydrogen; neutral sulphate of potassium would be K_2, SO_4; pyrophosphate of sodium, Na_4,P_2O_7; triphosphate of calcium, $Ca_3(PO_4)_2$. The acid salts would be those in which only part of the hydrogen is displaced by a metal; bisulphate of potassium would become K,H,SO_4, acid pyrophosphate of sodium, Na_2,H_2,P_2O_7. Double salts would be those in which the hydrogen is displaced by different metals; thus, alum $(K_2O.SO_3,Al_2O_3.3SO_3)$ would become $K_2,Al_2,4SO_4$, or $KAl2SO_4$; acid phosphate of potassium and sodium (K_2O,Na_2O,H_2O,P_2O_5) would be K,Na,H,PO_4. A serious objection to this view is, that it overlooks radicals now existing (as SO_3, P_2O_5, CO_2), and substitutes others which are not known to exist (as SO_4, PO_4, CO_3).

Many chemists now represent the acids and salts by these formulæ, without insisting upon their containing any definite compound radical, or being composed upon any particular type. Thus nitric acid is written HNO_3, without expressing an opinion as to the existence of NO_3 as an actual entity.

The following definitions are relied upon by those who adopt this course :—

An *acid* is a compound containing hydrogen, the whole or part of which is displaceable by a metal.

A *salt* is a compound derived from an acid by the displacement of its hydrogen by a metal.

A *monobasic acid* contains but one atom of displaceable hydrogen, and therefore can only form one series of salts.

A *dibasic acid* contains two atoms of displaceable hydrogen, and therefore can form two series of salts (normal and acid salts).

A *tribasic acid* contains three atoms of displaceable hydrogen, and therefore can form three series of salts (normal salts, and two series of acid salts).

A *normal salt* is one in which the whole of the displaceable hydrogen has been displaced by a metal.

An *acid salt* is one in which only part of the displaceable hydrogen has been displaced by a metal.

A *double salt* is one in which the displaceable hydrogen has been displaced by different metals.

A *basic salt* is a combination of a salt with a basic oxide.

A few examples may be collected here to illustrate these definitions:—

Monobasic Acids and Salts.

Nitric Acid, ...	HNO_3
Nitrate of potassium, ...	KNO_3
Metaphosphoric acid, ...	HPO_3
Metaphosphate of sodium, . . .	$NaPO_3$
Hypophosphorous acid, . . .	HPH_2O_2
Hypophosphite of sodium, . . .	$NaPH_2O_2$

Dibasic Acids and Salts.

Sulphuric acid, ...	H_2SO_4
Normal sulphate of potassium, . .	K_2SO_4
Acid „ „ . . .	$KHSO_4$
Phosphorous acid, ...	H_2PHO_3
Normal phosphite of sodium, . . .	Na_2PHO_3
Acid phosphite of barium, . . .	$BaH_2(PHO$

Tribasic Acids and Salts.

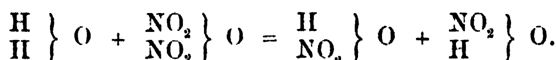
Orthophosphoric acid, . . .	H_3PO_4
Normal orthophosphate of sodium, . .	Na_3PO_4
Monacid orthophosphate (or common phosphate),	Na_2HPO_4
Diacid orthophosphate, . . .	NaH_2PO_4
Microcosmic salt, ...	$Na(NH_4)HPO_4$
Arsenic acid, ...	H_3AsO_4
Normal arseniate of sodium, . . .	Na_3AsO_4
Monacid arseniate „ . . .	Na_2HAsO_4
Diacid arseniate „ . . .	NaH_2AsO_4

To this view of the constitution of acids and salts, it may be objected that it presupposes the existence of a hydrogen compound corresponding in composition to the normal salt. Thus the carbonates would be derived from an imaginary carbonic acid of the formula H_2CO_3; the arsenites from an imaginary arsenious acid, H_3AsO_3, &c. Indeed, out of the *twenty-one* mineral acids which are of practical importance, there are *seven* which must be thus treated in order to accommodate this theory, viz., carbonic (CO_2), nitrous (N_2O_3), sulphurous (SO_2), arsenious (As_2O_3), chromic (CrO_3), hypochlorous (Cl_2O), and chlorous (Cl_2O_3). It must,

however, be acknowledged that no theory of the constitution of acids and salts has yet been advanced which is thoroughly supported on all sides by experimental evidence.

From what has been stated above, it will have been seen that an examination of the acid itself is by no means necessary in order to ascertain what its *basicity* is. If only one series of its salts can be discovered, it is a monobasic acid. If a normal and an acid salt (or a double salt) can be obtained, the acid is dibasic. When, beside the normal salt, there are two series of acid salts, the acid is tribasic.

Water-type theory of the constitution of salts.—Another ingenious theory of the constitution of salts is that known as the *water-type* theory, according to which all oxygen acids are fashioned after the type of water, by the displacement of its hydrogen by a compound radical, such displacement being total in the anhydrous acids, and partial in the hydrated acids. Then, a monobasic acid is formed upon the type of one molecule of water, by the displacement of one atom of hydrogen to form the (hydrated) acid, and of both atoms to form the (anhydrous acid or) anhydride. Thus nitric acid (HNO_3) would be written $\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O$, and *nitric anhydride* (N_2O_5) would become $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$; and nitrate of potassium (KNO_3) would be $\left.\begin{matrix}K\\NO_2\end{matrix}\right\}O$; a glance at these formulæ shows why a monobasic acid like nitric acid does not form either acid salts or double salts, because it contains only one atom of hydrogen, and therefore can only form a single salt with each metal by displacement of that hydrogen. This view does not ignore the existence of the anhydrous nitric acid, and assumes, as the radical of the acid, the substance NO_2, which has the composition of nitric peroxide. The formation of nitric acid by the action of water upon nitric anhydride would be thus expressed—



$$\left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O = \left.\begin{matrix}H\\NO_2\end{matrix}\right\}O + \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O.$$

In a similar manner, phosphoric anhydride (P_2O_5) would be represented by $\left.\begin{matrix}PO_2\\PO_2\end{matrix}\right\}O$, metaphosphoric acid ($HPO_3$) by $\left.\begin{matrix}H\\PO_2\end{matrix}\right\}O$, and the metaphosphate of sodium by $\left.\begin{matrix}Na\\PO_2\end{matrix}\right\}O$. In this case, however, the radical PO_2 is, so far as we know, imaginary.

A dibasic acid is one which is composed after the type of a double molecule of water, $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$, and therefore contains two atoms of hydrogen which may be displaced either entirely by a metal, yielding a normal salt, or partly by a metal, yielding an acid salt, or by two metals, yielding a double salt. For example, sulphuric acid ($H_2O.SO_3$) would be $\left.\begin{matrix}H_2\\SO_2''\end{matrix}\right\}O_2$, or two molecules of water, in which two atoms of hydrogen are displaced by the diatomic radical SO_2; normal sulphate of potassium $\left.\begin{matrix}K_2\\SO_2''\end{matrix}\right\}O_2$, acid sulphate of potassium (bisulphate of potash) $\left.\begin{matrix}KH\\SO_2''\end{matrix}\right\}O_2$ and sulphuric anhydride, $\left.\begin{matrix}SO_2''\\SO_2''\end{matrix}\right\}O_2$.

Here again the radical SO_2 has the same composition as sulphurous acid, which might well be accepted as the radical of sulphuric acid.

Again, carbonic anhydride would be $\left.\begin{matrix}CO''\\CO''\end{matrix}\right\}O_2$, the imaginary carbonic acid, $\left.\begin{matrix}H_2\\CO''\end{matrix}\right\}O_2$, carbonate of potassium, $\left.\begin{matrix}K_2\\CO''\end{matrix}\right\}O_2$, acid carbonate of potassium, $\left.\begin{matrix}KH\\CO''\end{matrix}\right\}O_2$, carbonate of potassium and sodium, $\left.\begin{matrix}KNa\\CO''\end{matrix}\right\}O_2$.

The radical of carbonic acid, therefore (CO), would have the same composition as carbonic oxide, which is seen to have a diatomic character in its compound with chlorine, $(CO)''Cl_2$, where it occupies the place of two atoms of hydrogen.

In applying this view to pyrophosphoric acid ($2H_2O.P_2O_5 = H_4P_2O_7$), some difficulty arises because its formula cannot be written on the type of two molecules of water (H_4O_2) on account of the indivisibility of the O_7 into two whole numbers; it is therefore necessary to take four molecules of water as the type, when we have—

Type, $\left.\begin{matrix}H_4\\H_4\end{matrix}\right\}O_4$, pyrophosphoric acid, $\left.\begin{matrix}H_4\\(P_2O_3)''''\end{matrix}\right\}O_4$, pyrophosphate of sodium, $\left.\begin{matrix}Na_4\\(P_2O_3)''''\end{matrix}\right\}O_4$, acid pyrophosphate of sodium, $\left.\begin{matrix}Na_2H_2\\(P_2O_3)''''\end{matrix}\right\}O_4$.

Here the increased complexity of the formulæ appears objectionable.

A few salts are known in which two acids are combined with the same base, such as the acetonitrate of baryta, composed of nitrate and acetate of baryta. It is obvious that the same reasoning which leads to the conclusion that an acid capable of forming a double salt with two different bases is dibasic, or contains a diatomic acid radical, would also support the inference that a base capable of forming a double salt with two different acids is di-acid, or contains a diatomic basic radical. Hence the existence of the above acetonitrate of baryta countenances the belief that barium is a diatomic metal. The formula of the salt would then be written, on the type of two molecules of water, thus—$\left.\begin{matrix}Ba''\\(C_2H_3O)'\\(NO_2)'\end{matrix}\right\}O_2$.

A tribasic acid is formed upon the type of a treble molecule of water, thus—

Type, $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$, tribasic phosphoric acid, $\left.\begin{matrix}H_3\\PO'''\end{matrix}\right\}O_3$, triphosphate of sodium, $\left.\begin{matrix}Na_3\\PO'''\end{matrix}\right\}O_3$, common phosphate of sodium, $\left.\begin{matrix}Na_2H\\PO'''\end{matrix}\right\}O_3$, microcosmic salt (phosphate of sodium and ammonium), $\left.\begin{matrix}Na(NH_4)'H\\PO'''\end{matrix}\right\}O_3$.

But in this case also an unknown radical, PO, is assumed.

If pyrophosphoric acid be represented by $\left.\begin{matrix}H_4\\(PO)'''(PO_2)'\end{matrix}\right\}O_4$ its intermediate position between metaphosphoric acid $\left.\begin{matrix}H\\PO_2'\end{matrix}\right\}O$, and orthophosphoric acid $\left.\begin{matrix}H_3\\PO'''\end{matrix}\right\}O_3$ is at once apparent.

CHEMISTRY OF THE METALS.

180. The general principles of chemistry having been explained and illustrated in the history of the non-metallic elements, the chemistry of the metals will be discussed with less attention to details, which, however interesting in a strictly chemical sense, are not, at present, of immediate practical importance.

The definition of a metal has been already given at p. 27, as *an element capable of forming a base by union with oxygen.*

POTASSIUM.

K′ = 39 parts by weight.

The indispensable alkali, *potash*, appears to have been originally derived from the granitic rocks, where it exists in combination with silicic acid and alumina, in the well-known minerals, *feldspar* and *mica*. These rocks having, in course of time, disintegrated to form soils for the support of plants, the potash has been converted into a soluble state, and has passed into the plants as a necessary portion of their food.

In the plant, the potash is found to have entered into various forms of combination; thus, most plants contain sulphate of potash and chloride of potassium; but the greater portion of the potash exists in combination with certain vegetable acids formed in the plant, and when the latter is burnt, the salts of potash with the vegetable acids are decomposed by the heat, leaving the potash in combination with carbonic acid, forming carbonate of potash ($K_2O.CO_2$).

Carbonate of potash.—When the ashes of plants are treated with water, the salts of potash are dissolved, those of lime and magnesia being left. On separating the aqueous solution and evaporating it to a certain point, a great deal of the sulphate of potash, being much less soluble, is deposited, and the carbonate of potash remains in the solution; this is evaporated to dryness, when the carbonate of potash is left, mixed with much chloride of potassium, and some sulphate of potash; this mixture constitutes the substances imported from America and other countries where wood is abundant, under the name of *potashes*, which are much in demand for the manufacture of soap and glass. When further purified, these are sold under the name of *pearlash*, but this is still far from being pure carbonate of potash.

During the fermentation of the grape-juice, in the preparation of wine, a hard crystalline substance is deposited, which is known in commerce by the name of *argol*, or when purified, as *cream of tartar*. The chemical

name of this salt is bitartrate of potash, for it is derived from potash and tartaric acid, a vegetable acid having the composition $H_2O.C_4H_4O_5$. When this salt ($K_2O.H_2O.2C_4H_4O_5$) is heated, the tartaric acid is decomposed into a variety of products, among which are found carbonic acid, which remains in combination with the potash, and carbon, which is left mixed with the carbonate of potash; but if the heat be continued, and free access of air permitted, the carbon will be entirely burnt away, and carbonate of potash will be left (*salt of tartar*).

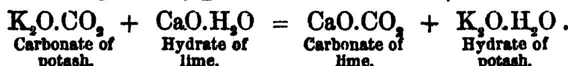
In wine-producing countries, carbonate of potash is prepared from the refuse yeast which rises during the fermentation, and is dried in the sun in order to be subsequently incinerated.

The fleeces of sheep contain a considerable proportion of potash combined with an animal acid; when the fleece is washed with water, the salt of potash is dissolved out, and on evaporating the liquid and burning the residue, it is converted into carbonate of potash.

Hydrate of potash ($K_2O.H_2O$, or KHO).—Carbonate of potash was formerly called potash, and was supposed to be an elementary substance. It was known that its alkaline qualities were rendered far more powerful by treating it with lime, which caused it to be termed *mild* alkali, in order to distinguish it from the *caustic** alkali obtained by means of lime, and possessed of very powerful corrosive properties. Lime, it was said, is derived from limestone by the action of fire, and therefore owes its peculiar properties to the acquisition of a certain amount of the matter of fire, which, in turn, it imparts to the mild alkali, and thus confers upon it a caustic or burning power.

Black's researches in the middle of the eighteenth century, which are often referred to as models of inductive reasoning, exposed the fallacy of this explanation, and proved that instead of acquiring anything from the fire, the limestone actually lost carbonic acid, and instead of imparting anything to the mild alkali, the lime really gained as much carbonic acid as it had previously lost.

The caustic potash, so largely employed by the soap-maker, is obtained by adding slaked lime to a boiling diluted solution of the carbonate of potash, when the water of the hydrate of lime is exchanged for the carbonic acid, and the carbonate of lime is deposited at the bottom of the vessel, whilst *hydrate of potash* remains in the clear solution—



$$K_2O.CO_2 + CaO.H_2O = CaO.CO_2 + K_2O.H_2O.$$

If the solution of carbonate of potash be too strong, the lime will not remove the whole of the carbonic acid.

When the solution is evaporated, the hydrate of potash remains as a clear oily liquid, which solidifies to a white mass as it cools, and forms the fused potash of commerce, which is often cast into cylindrical sticks for more convenient use.† The hydrate of potash is the most powerful alkaline substance in ordinary use, and is very frequently employed by the chemist on account of its energetic attraction for the different acids. It is generally used in the state of solution, the strength of which is inferred from its specific gravity, this being higher in proportion to the amount of potash contained in the solution.

* From καιω, to burn.
† These have sometimes a greenish colour, due to the presence of some manganate of potash.

Potassium.—Of the composition of hydrate of potash nothing was known till the year 1807, when Davy succeeded in decomposing it by the galvanic battery; this experiment, which deserves particular notice, as being the first of a series resulting in the discovery of so many important metals, was made in the following manner:—a fragment of hydrate of potash, which, in its dry state, does not conduct electricity, was allowed to become slightly moist by exposure to the air, and placed upon a plate of platinum attached to the positive (copper) end of a very powerful galvanic battery; when the wire connected with the negative (zinc) end was made to touch the surface of the hydrate of potash, some small metallic globules resembling mercury made their appearance at the extremity of this (negative) wire, at which the hydrogen contained in the hydrate of potash was also eliminated, whilst bubbles of oxygen were separated on the surface of the platinum plate connected with the positive wire (see p. 5). By allowing the negative wire to dip into a little mercury contained in a cavity upon the surface of the potash, a combination of potassium with mercury was obtained, and the mercury was afterwards separated by distillation. This process, however, furnished the metal in very small quantities, and, though it was obtained with greater facility a year or two afterwards by decomposing hydrate of potash with white-hot iron, some years elapsed before any considerable quantity of potassium was prepared by the present method of distilling in an iron retort an intimate mixture of carbonate of potash and carbon, obtained by calcining cream of tartar; in this process the oxygen of the potash is removed by the carbon in the form of carbonic oxide ($K_2O.CO_2 + C_2 = K_2 + 3CO$).

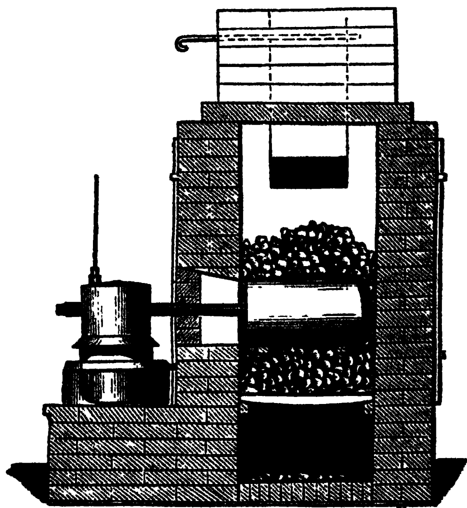


Fig. 234.—Preparation of potassium.

The annexed figure represents the iron retort connected with its copper receiver, surrounded with cold water, and containing petroleum to protect the distilled potassium from oxidation. The lateral tube of the receiver permits the tube of the retort to be cleared, if necessary, during the distillation, by the passage of an iron rod.

Some of the most striking properties of this metal have already been referred to (p. 10); its softness, causing it to be easily cut like wax, the rapidity with which its silvery surface tarnishes when exposed to the air, its great lightness (sp. gr. 0·865), causing it to float upon water, and its taking fire when in contact with that liquid, sufficiently distinguish it from other metals. It fuses easily when heated, and is converted, at a higher temperature, into a green vapour; if air be present, it burns with a violet-coloured flame, and is converted into *anhydrous potash*, the oxide of potassium (K_2O).

The property of burning with this peculiar violet-coloured flame is

characteristic of potassium, and allows it to be recognised in its compounds.

If a solution of nitrate of potash (saltpetre) in water be mixed with enough spirit of wine to allow of its being inflamed, the flame will have a peculiar lilac colour. This colour may also be developed by exposing a very minute particle of saltpetre, taken on the end of a heated platinum wire, to the reducing (inner) blowpipe flame (fig. 235), when the potassium, being reduced to the metallic state, and passing into the oxidising (outer) flame in the state of vapour, imparts to that flame a lilac tinge.

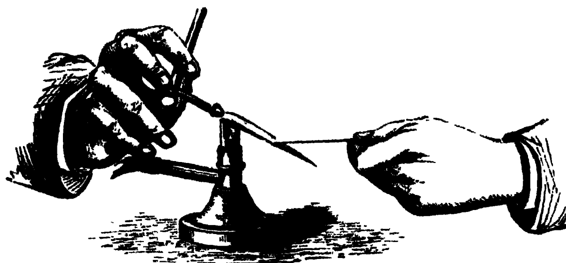


Fig. 235. --Coloured flame test.

The difficulty and expense attending the preparation of potassium have prevented its receiving any application except in purely chemical operations, where its attraction for oxygen, chlorine, and other electronegative elements, is often turned to account.

The *chloride of potassium* (KCl) is an important natural source of this metal, being extracted from sea-water, from kelp (the ash of sea-weed), and from the refuse of the manufacture of sugar from beet-root. It also occurs in combination with chloride of magnesium, forming the mineral known as *carnallite* ($K_2Cl.MgCl_2.6H_2O$), an immense saline deposit overlying the rock-salt in the salt-mines of Stassfurth in Saxony. Carnallite resembles rock-salt in appearance, but is very deliquescent; it promises to become the most important source of potassium hitherto discovered.

Bicarbonate of potash ($K_2O.H_2O.2CO_2$, or $KHCO_3$), which is much used in medicine, is obtained by passing carbonic acid through a strong solution of carbonate of potash, when it is deposited in crystals, being much less soluble in water than the normal carbonate.

Nitrate of potash ($K_2O.N_2O_5$, or KNO_3), or *saltpetre*, will be specially considered in the section on gunpowder.

The following less important compounds of potassium have not been noticed elsewhere, and are not of sufficient practical importance to require particular description in this work:—

Peroxide of potassium,	K_2O_2	Sesquisulphide of potassium,	K_2S_3
Monosulphide ,,	K_2S	Tetrasulphide ,,	K_2S_4
Disulphide ,,	K_2S_2	Pentasulphide ,,	K_2S_5

SODIUM.

Na′ = 23 parts by weight.

181. Sodium is often found, in place of potassium, in the feldspars and other minerals, but we are far more abundantly supplied with it in the form of *common salt* (chloride of sodium, NaCl), occurring not only in the solid state, but dissolved in sea-water, and in smaller quantity in the waters derived from most lakes, rivers, and springs.

Rock-salt forms very considerable deposits in many regions; in this country the most important is situated at Northwich in Cheshire, where very large quantities are extracted by mining. Wielitzka, in Poland, is celebrated for an extensive salt mine, in which there are a chapel and dwelling-rooms, the furniture of which is made of this rock. Extensive beds of rock-salt also occur in France, Germany, Hungary, Spain, Abyssinia, and Mexico. Perfectly pure specimens form beautiful colourless cubes, and are styled *sal gem*; but ordinary rock-salt is only partially transparent, and exhibits a rusty colour, due to the presence of iron. In some places the salt is extracted by boring a hole into the rock and filling it with water, which is pumped up when saturated with salt, and evaporated in boilers, the minute crystals of salt being removed as they are deposited.

At Droitwich, in Worcestershire, the salt is obtained by evaporation from the waters of certain salt springs. In some parts of France and Germany the water from the salt springs contains so little salt that it would not pay for the fuel necessary to evaporate the water, and a very ingenious plan is adopted, by which the proportion of water is greatly reduced without the application of artificial heat. For this purpose a lofty scaffolding is erected and filled with bundles of brushwood, over which the salt water is allowed to flow, having been raised to the top of the scaffolding by pumps. In trickling over the brushwood this water exposes a large surface to the action of the wind, and a considerable evaporation takes place, so that a much stronger brine is collected in the reservoir beneath the scaffolding; by several repetitions of the operation, the proportion of water is so far diminished that the rest may be economically evaporated by artificial heat. The brine is run into boilers and rapidly boiled for about thirty hours, fresh brine being allowed to flow in continually, so as to maintain the liquid at the same level in the boiler. During this ebullition a considerable deposit, composed of the sulphates of lime and soda, is formed, and raked out by the workmen. When a film of crystals of salt begins to form upon the surface, the fire is lowered and the temperature of the brine allowed to fall to about 180° F., at which temperature it is maintained for several days whilst the salt is crystallising. The crystals are afterwards drained and dried by exposure to air. The grain of the salt is regulated by the temperature at which it crystallises, the size of the crystals increasing as the temperature falls. It is not possible to extract the whole of the salt in this way, since the last portions which crystallise will always be contaminated with other salts present in the brine, but the *mother-liquor* is not wasted, for after as much salt as possible has been obtained, it is made to yield sulphate of soda (Glauber's salt), sulphate of magnesia (Epsom salts), bromine and iodine.

The process adopted for extracting the salt from sea-water depends upon the climate. In Russia, shallow pits are dug upon the shore, in

which the sea-water is allowed to freeze, when a great portion of the water separates in the form of pure ice, leaving a solution of salt sufficiently strong to pay for evaporation.

Where the climate is sufficiently warm, the sea-water is allowed to run very slowly through a series of shallow pits upon the shore, where it becomes concentrated by spontaneous evaporation, and is afterwards allowed to remain for some time in reservoirs in which the salt is deposited. The coarse crystals thus obtained are known in commerce as *bay-salt.* Before they are sent into the market they are allowed to drain for a long time, in a sheltered situation, when the chloride of magnesium with which they are contaminated deliquesces in the moisture of the air and drains off. The *bittern,* or liquor remaining after the salt has been extracted, is employed to furnish magnesia and bromine.

Great improvements have been made during the last few years in the economical extraction of the salts from sea-water. It will be remembered that 1000 parts of sea-water contain about

29·0 parts of chloride of sodium,
0·5 ,, chloride of potassium,
3·0 ,, chloride of magnesium,
2·5 ,, sulphate of magnesia,
1·5 ,, sulphate of lime, &c.

In a warm climate, that of Marseilles, for example, the water is allowed to evaporate spontaneously until it has a specific gravity of 1·24. During this evaporation it deposits about four-fifths of its chloride of sodium. It is then mixed with one-tenth of its volume of water and artificially cooled to 0° F. (see p. 123), when it deposits a quantity of sulphate of soda, resulting from the decomposition of part of the remaining chloride of sodium by the sulphate of magnesia. The mother-liquor is evaporated down till its specific gravity is 1·33, a fresh quantity of chloride of sodium being deposited during the evaporation. When the liquid cools it deposits a double salt composed of chloride of potassium and chloride of magnesium, from which the latter may be extracted by washing with a very little water, leaving the chloride of potassium fit for the market.

This process is instructive as illustrating the influence exerted upon the arrangement of the various acids and bases in a saline solution by the temperature to which the solution is exposed, the general rule being that a salt is formed which is insoluble in the liquid at that particular temperature.

The great tendency observed in ordinary table salt to become damp when exposed to the air, is due chiefly to the presence of small quantities of chloride of magnesium and chloride of calcium, for pure chloride of sodium has very much less disposition to attract atmospheric moisture, although it is very easily dissolved by water, 2¾ parts of this liquid being able to dissolve one part (by weight) of salt.

In the history of the useful applications of common salt, is to be found one of the best illustrations of the influence of chemical research upon the development of the resources of a country, and a capital example of a manufacturing process not based, as such processes usually are, upon mere experience, independent of any knowledge of chemical principles, but upon a direct and intentional application of these to the attainment of a particular object.

Until the last quarter of the eighteenth century, the uses of common salt were limited to culinary and agricultural purposes, and to the glazing of the coarser kinds of earthenware, whilst a substance far more useful in the arts, *carbonate of soda,* was imported chiefly from Spain under the name of *barilla,* which was the ash obtained by burning a marine plant known as the *salsola soda.* But this ash only contained about one-fourth

of its weight of carbonate of soda, so that this latter substance was thus imported at a great expense, and the manufactures of soap and glass to which it is indispensable were proportionally fettered.

During the wars of the French Revolution the price of barilla had risen so considerably, that it was deemed advisable by Napoleon to offer a premium for the discovery of a process by which the carbonate of soda could be manufactured at home, and to this circumstance we are indebted for the discovery, by Leblanc, of the process at present in use for the manufacture of carbonate of soda from common salt, a discovery which placed this substance at once among the most important raw materials with which a country could be furnished.

182. *Manufacture of carbonate of soda from common salt.*—The salt is spread upon the hearth of a *reverberatory* furnace (fig. 236),* and mixed



Fig. 236.—Furnace for converting common salt into sulphate of soda.

with an equal weight of sulphuric acid, which converts it into the sulphate of soda (p. 153), expelling the hydrochloric acid in the form of gas, which would prove highly injurious to the vegetation in the neighbourhood, and is therefore usually condensed by being brought into contact with water (see p. 154). The flame of the fire is allowed to play over the surface of the mixture of salt and sulphuric acid until it has become perfectly dry; in this state it is technically known as *salt-cake*, and is next mixed with about an equal weight of limestone and rather more than half its weight of small coal; this mixture is again heated upon the hearth of a reverberatory furnace, when it evolves an abundance of carbonic oxide, and yields a mixture of carbonate of soda with lime and sulphide of calcium; this mixture is technically known as *black-ash*.

The change which has been effected in the sulphate of soda will be easily understood; for when this salt is heated in contact with carbon (from the small coal) it loses its oxygen, and becomes sulphide of sodium, whilst carbonic acid is evolved; thus—



$$Na_2O.SO_3 + C_2 = Na_2S + 2CO_2.$$

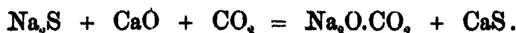
* The hearth of this furnace is usually divided, as seen in the figure, into two compartments, in one of which (lined with lead), more remote from the grate, the decomposition is effected, the acid being poured in through the funnel, while in that nearest to the grate, lined with fire-brick, the whole of the hydrochloric acid is expelled, and the sulphate of soda fused.

Again, when carbonate of lime is heated in contact with carbon, carbonic oxide is given off, and lime remains—



$$CaO.CO_2 + C = 2CO + CaO.$$

Finally, when sulphide of sodium and lime are heated together in the presence of carbonic acid, carbonate of soda and sulphide of calcium are produced—



$$Na_2S + CaO + CO_2 = Na_2O.CO_2 + CaS.$$

When the black ash is treated with water, the carbonate of soda is dissolved, leaving the sulphide of calcium, and by evaporating the solution, ordinary *soda ash* is obtained. But this is by no means pure carbonate of soda, for it contains, in addition to a considerable quantity of common salt and sulphate of soda, a certain amount of caustic soda or hydrate of soda, formed by the action of the excess of lime upon the carbonate of soda. In order to purify it, the crude soda ash is mixed with small coal or sawdust and again heated, when the carbonic acid formed from the carbonaceous matter converts the hydrate of soda into carbonate, and on dissolving the mass in water and evaporating the solution, it deposits oblique rhombic prisms of common washing soda, having the composition, $Na_2O.CO_2.10Aq.$ (*soda crystals*).

A little reflection will show the important influence which this process has exerted upon the progress of the useful arts in this country. The three raw materials, salt, coal, and limestone, we possess in abundance. The sulphuric acid, when the process was first introduced, bore a high price, but the resulting demand for this acid gave rise to so many improvements in its manufacture that its price has been very greatly diminished,—a circumstance which has, of course, produced a most beneficial effect upon all branches of manufacture in which the acid is employed.

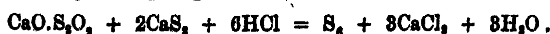
The large quantity of hydrochloric acid obtained as a secondary product has been employed for the preparation of bleaching powder, and the important arts of bleaching and calico-printing have thence received a considerable impulse. These arts have also derived a more direct benefit from the increased supply of carbonate of soda, which is so largely used for cleansing all kinds of textile fabrics. The manufactures of soap and glass, which probably create the greatest demand for carbonate of soda, have been increased and improved beyond all precedent by the production of this salt from native sources.

Recovery of sulphur from alkali-waste.—Since nearly the whole of the sulphur which is employed, in the form of sulphuric acid, for decomposing the common salt, is obtained at the alkali-works in the form of sulphide of calcium in the *tank-waste* left after exhausting the black ash with water, several processes have been devised for recovering the sulphur in order to employ it again for the manufacture of oil of vitriol. The simplest of these consists in blowing air through the moist tank-waste, until it is converted into a mixture of bisulphide of calcium and hyposulphite of lime, the oxidation being stopped when one-third of the bisulphide of calcium has been converted into hyposulphite.



$$(1.)\ 2CaS + O = CaO + CaS_2. \quad (2.)\ CaS_2 + O_3 = CaO.S_2O_2.$$

When the yellow liquor thus obtained is decomposed by the muriatic acid from the alkali-works, the sulphur is precipitated;



$$CaO.S_2O_2 + 2CaS_2 + 6HCl = S_6 + 3CaCl_2 + 3H_2O.$$

An objection to this process appears to be the difficulty in procuring a sufficient

quantity of muriatic acid, for which there is a great demand on the part of the producers of bleaching powder and bicarbonate of soda.

Another process for recovering the soda employs the waste liquor from the chlorine stills (see p. 144), which contains chloride of manganese ($MnCl_2$) and perchloride of iron (Fe_2Cl_6). On treating the sulphide of calcium in the soda-waste with this still liquor, chloride of calcium and sulphides of iron and manganese are produced;



$$MnCl_2 + CaS = MnS + CaCl_2; \quad Fe_2Cl_6 + 3CaS = Fe_2S_3 + 3CaCl_2.$$

By exposing these sulphides to the air, in a moist state, the sulphur is separated, and the metals are converted into oxides.



$$2MnS + O_3 = Mn_2O_3 + S_2; \quad Fe_2S_3 + O_3 = Fe_2O_3 + S_3.$$

By stirring these oxides with more soda-waste, the sulphides are reproduced; and are afterwards again oxidised by exposure to air, so as to separate their sulphur. The sulphur thus separated combines with the sulphide of calcium in a fresh portion of the waste, to form a bisulphide, one-third of which is oxidised by the air, as in the process first described, and converted into hyposulphite of lime. In order to precipitate the sulphur from the liquor containing the bisulphide of calcium and hyposulphite of lime, the excess of hydrochloric acid always present in the chlorine still liquor is turned to account; the sulphur liquor is run into this until the precipitated sulphur begins to be accompanied by a black precipitate of sulphide of iron, showing that all the free acid has been neutralised. The still liquor thus neutralised is then employed for decomposing a fresh portion of the soda-waste as at the commencement of the process. The precipitated sulphur is pressed to free it from the liquor, dried, and melted by super-heated steam.

Although the chemistry of this process is rather elaborate, the practical working is said to be very simple and inexpensive.

The crystals of carbonate of soda are easily distinguished by their property of efflorescing in dry air (p. 41), and by their alkaline taste, which is much milder than that of carbonate of potash, this being, moreover, a deliquescent salt. The crystals are very soluble in water, requiring only 2 parts of cold and less than their own weight of boiling water; the solution is strongly alkaline to test papers.

The substance commonly used in medicine under the name of carbonate of soda, is really the *bicarbonate* ($Na_2O.CO_2.H_2O.CO_2$ or $NaHCO_3$), and is prepared by saturating the carbonate of soda with carbonic acid gas. It is readily distinguished from the carbonate, as it is but slightly alkaline, and is very much less easily dissolved by water.

Soda lye, employed in the manufacture of hard soap, is a solution of *hydrate of soda* ($Na_2O.H_2O$ or $NaHO$), obtained by decomposing the carbonate of soda with hydrate of lime (slaked lime, $CaO.H_2O$), when the water of this latter compound is exchanged for the carbonic acid of the carbonate.

The solid hydrate of soda of commerce is generally obtained in the process for manufacturing carbonate of soda, just described; the solution obtained by treating the black ash with water is concentrated by evaporation, so that the carbonate and sulphate of soda and chloride of sodium may crystallise out, leaving the hydrate of soda, which is far more soluble, in the liquid. The latter, which still contains a compound of sulphide of sodium and sulphide of iron, which gives it a red colour, is mixed with some nitrate of soda to oxidise the sulphides, and evaporated down until a fused mass of hydrate of soda is left, which is poured out into iron moulds.*

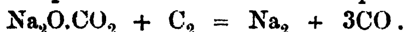
* Another plan of treating the black ash liquor consists in allowing it to trickle through a column of coke against a current of air, when the sulphide of sodium (Na_2S) is oxidised and converted into soda (Na_2O) and hyposulphite of soda ($Na_2S_2O_3$), whilst the sulphide of iron is deposited. The liquor is mixed with a little chloride of lime to oxidise any remaining sulphides, and concentrated by evaporation, when carbonate of soda and ferrocyanide of sodium are deposited in crystals. The liquor separated from these contains the hydrate of soda, and is evaporated till it solidifies on cooling.

Kryolite ($3NaF.AlF_3$) is sometimes employed as a source of the sodium for hydrate of soda, which may be obtained by decomposing it with hydrate of lime.

183. *Sodium.*—Potash and soda exhibit so much similarity in their properties, that we cannot be surprised at their having been confounded together by the earlier chemists, and it was not till 1736 that Du Hamel pointed out the difference between them. The discovery of potassium naturally led Davy to that of sodium, which can be obtained by processes exactly similar to those adopted for procuring potassium, to which it will be remembered sodium presents very great similarity in properties (p. 11). Sodium, however, is readily distinguished from potassium by its burning with a yellow flame, which serves even to characterise it when in combination.

This yellow flame is well seen by dissolving salt in water in a plate, and adding enough spirit of wine to render it inflammable, the mixture being well stirred while burning. If a little piece of sodium be burnt in an iron spoon held in a flame, all the flames in the room, even at a remote distance, will be tinged yellow. The blowpipe flame may also be employed to detect sodium by this colour, as in the case of potassium (p. 260). In fireworks, nitrate of soda is employed for producing yellow flames. A very good *yellow fire* may be made by intimately mixing, in a mortar, 74 grs. of nitrate of soda, 20 grs. of sulphur, 6 grs. of sulphide of antimony, and 2 grs. of charcoal, all carefully dried, and very finely powdered.

The preparation of sodium, by distilling a mixture of carbonate of soda and charcoal, is much easier than that of potassium, for which reason sodium is far less costly than that metal, and has received applications, on the large scale, during the last few years, for the extraction of the metals aluminum and magnesium. An amalgam of sodium (p. 126) is also employed with advantage in extracting gold and silver from their ores. To obtain sodium in large quantity, a mixture of dried carbonate of soda, powdered coal, and chalk, is distilled in iron cylinders, when the oxygen of the soda is abstracted by the carbon, which it converts into carbonic oxide, and the sodium passes over in the form of vapour.



$$Na_2O.CO_2 + C_2 = Na_2 + 3CO.$$

The chalk is employed to prevent the fusion of the mixture.

184. *Borax, biborate of soda* ($Na_2O.2B_2O_3$).—A very important compound of soda is used in the arts under the name of *borax*, in which the soda is combined with boracic acid. It has already been stated that this substance is deposited during the evaporation of the waters of certain lakes in Thibet, whence it is imported into this country in impure crystals, which are covered with a peculiar greasy coating. The refiner of tincal powders the crystals and washes them, upon a strainer, with a weak solution of soda, which converts the greasy matter into a soap and dissolves it. The borax is then dissolved in water, a quantity of carbonate of soda is added to separate some lime which the borax usually contains, and, after filtering off the carbonate of lime, the solution is evaporated to the crystallising point and allowed to cool, in order that it may deposit the pure crystals of borax.

It appears, however, that the greater part of the borax employed in the arts is manufactured in this country by heating carbonate of soda with boracic acid, when the latter expels the carbonic acid and combines with the soda.* The mass is then dissolved in water, and the borax crystal-

* The ammonia which is evolved from the Tuscan boracic acid employed in this process is known in commerce as *Volcanic ammonia*, and is free from the empyreumatic odour which generally accompanies that from coal and bones.

lised, an operation upon which much care is bestowed, since the product does not meet with a ready sale unless in large crystals.

The solution of borax, having been evaporated to the requisite degree of concentration, is allowed to crystallise in covered wooden boxes, which are lined with lead and enclosed in an outer case of wood, the space between the sides of the case and the box being stuffed with some bad conductor of heat, so that the solution of borax may cool very slowly, and large crystals may be deposited. In about thirty hours the crystallisation is completed, when the liquid is drawn off as rapidly as possible, the last portion being carefully soaked up with sponges, so that no small crystals may be afterwards formed upon the surface of the large ones; the case is then again covered up, so that the crystals may cool slowly without cracking.

Borax is chemically known as *biborate of soda*, and is represented, in the dry state, by the formula $Na_2O.2B_2O_3$. The ordinary prismatic crystals, however, contain ten molecules of water of crystallisation, and are, therefore, represented by the formula $Na_2O.2B_2O_3.10Aq$. They soon effloresce and become opaque when exposed to air, and may readily be distinguished by their alkaline taste and action upon test-papers, and especially by their behaviour when heated, for they fuse easily and *intumesce* most violently, swelling up to a white spongy mass of many times their original bulk; this mass afterwards fuses down to a clear liquid which forms a transparent glassy mass on cooling (*vitrified borax*), and since this glass is capable of dissolving many metallic oxides with great readiness (borax being, by constitution, an acid salt, and therefore ready to combine with more base), it is much used in the metallurgic arts. Large quantities of borax are also employed in glazing stoneware.

185. *Silicate of soda.*—A combination of soda with silicic acid has long been used, under the name of *soluble glass*, for imparting a fire-proof character to wood and other materials, and, more recently, for producing artificial stone for building purposes, and for a peculiar kind of permanent fresco-painting (*stereochromy*), the results of which are intended to withstand exposure to the weather.

Soluble glass is usually prepared by fusing 15 parts of sand with 8 parts of carbonate of soda and 1 part of charcoal. The silicic acid, combining with the soda, disengages the carbonic acid, the expulsion of which is facilitated by the presence of charcoal, which converts it into carbonic oxide. The mass thus formed is scarcely affected by cold water, but dissolves when boiled with water, yielding a strongly alkaline liquid.

In using this substance for rendering wood fire-proof, a rather weak solution is first applied to the wood, and over this a coating of lime-wash is laid, a second coating of soluble glass (in a more concentrated solution) is then applied. The wood so prepared is, of course, charred, as usual, by the application of heat, but its inflammability is remarkably diminished.

For the manufacture of *Ransome's artificial stone*, the soluble glass is prepared by heating flints, under pressure, with a strong solution of hydrate of soda, to a temperature between 300° and 400° F., when the silicic acid constituting the flint enters into combination with the soda. Finely divided sand is moistened with this solution, pressed into moulds, dried, and exposed to a high temperature, when the silicate of soda fuses and cements the grains of sand together into a mass of artificial sandstone, to

which any required colour may be imparted by mixing metallic oxides with the sand before it is moulded.

Silicate of soda is also sometimes used as a *dung substitute* (p. 246) in calico-printing.

Sulphate of soda forms the very common saline efflorescence upon the surface of brick walls, and has been found covering the sandy soil of the Desert of Atacama, over a considerable area. The mineral known as *Thénardite* also consists of sulphate of soda, and *Glauberite* is a double sulphate of soda and lime ($Na_2O.SO_3$, $CaO.SO_3$) which is nearly insoluble in water.

Phosphate of soda ($2Na_2O.H_2O.P_2O_5.24Aq.$) is obtained by neutralising, with carbonate of soda, the impure phosphoric acid obtained by decomposing bone-ash with sulphuric acid (p. 231). On evaporation, the phosphate is deposited in oblique rhombic prisms which effloresce in air.

Nitrate of soda ($Na_2O.N_2O_5$ or $NaNO_3$) will be more particularly noticed in the section on gunpowder. It is imported from Peru, and used in considerable quantity as a manure, and for the manufacture of nitrate of potash.

SALTS OF AMMONIA.

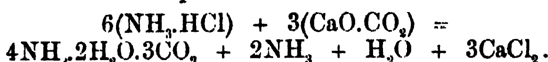
186. The great chemical resemblance between some of the salts of ammonia and those of potash and soda has been already pointed out as affording a reason for the hypothesis of the existence of a compound metal, *ammonium* (NH_4), equivalent in its functions to potassium and sodium. However convenient this assumption may be for the purpose of representing by equations the chemical changes in which the salts of ammonia take part, it is evidently necessary to place these salts on a different footing from those of potash and soda, until either the metal itself or its oxide $(NH_4)_2O$, which is at present equally hypothetical, shall be obtained. This has become the more necessary since modern chemistry has brought to light certain organic bases which exhibit a stronger resemblance to potash and soda than that evinced by ammonia, rendering it necessary to extend to these also the hypothesis of the existence of compound metals, and thus to encumber chemical pages with the names of a large class of substances of the existence of which there is no direct evidence.

Much encouragement has been afforded to the belief in the existence of oxide of ammonium $(NH_4)_2O$, by the circumstance that the compounds which are formed when ammonia (NH_3) combines with the anhydrous acids, such as carbonic (CO_2) and sulphuric (SO_3), do not exhibit the resemblance to the salts of potash and soda until water is added, the elements of which are required to convert $(NH_3)_2$ into $(NH_4)_2O$. Thus, by the action of dry ammonia gas upon anhydrous sulphuric acid, a compound called *sulphuric ammonide* is formed, having the composition $(NH_3)_2.SO_3$. This substance dissolves in water and crystallises in octahedra, but its solution is not precipitated by chloride of barium, which always precipitates the true sulphates, nor by chloride of platinum, which precipitates the true salts of ammonia. By long boiling with water, however, it becomes converted into the sulphate of ammonia, $2NH_3.H_2O.SO_3$ (or sulphate of oxide of ammonium, $(NH_4)_2O.SO_3$, which yields precipitates with both the above tests. The anhydrous phosphoric, carbonic, and sulphurous acids also combine with dry ammonia to form ammonides, which do not

respond to the ordinary tests for the corresponding salts of ammonia until after water has been assimilated. The true salts of ammonia are produced either by the combination of a hydrated acid with ammonia, or by double decomposition.

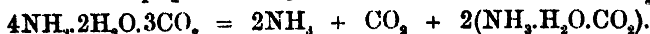
187. *Sulphate of ammonia* ($2NH_3.H_2O.SO_3$, or $(NH_4)_2SO_4$) is largely employed in the preparation of ammonia-alum, and of artificial manures, for which purposes it is generally obtained from the ammoniacal liquor of the gas-works by neutralising with sulphuric acid and evaporating. The rough crystals are gently heated to expel tarry substances, and purified by recrystallisation. The crystals have the same shape as those of sulphate of potash, and are easily soluble in water. When heated to about 500° F. the sulphate of ammonia is decomposed, yielding vapour of sulphite of ammonia ($2NH_3.H_2O.SO_2$), water, ammonia, nitrogen, and sulphurous acid. If muslin be dipped into a solution of sulphate of ammonia in ten parts of water, and dried, it will no longer burn with flame when ignited. The mineral *mascagnine* consists of sulphate of ammonia. This salt is occasionally found in needle-like crystals upon the windows of rooms in which coal-gas is burnt. The *bisulphate of ammonia* contains $NH_3.H_2O.SO_3$, or NH_4HSO_4.

188. *Sesquicarbonate of ammonia* ($4NH_3.2H_2O.3CO_2$, or $2(NH_4)_2O.3CO_2$) is the common carbonate of ammonia of the shops, also called *smelling salts* or *Preston salts*, largely used in medicine, and by bakers and confectioners, for imparting lightness or porosity to cakes, &c. It is commonly prepared by mixing sal-ammoniac (hydrochlorate of ammonia) with twice its weight of chalk, and distilling the mixture in an earthen or iron retort communicating, through an iron pipe, with a leaden chamber or receiver, in which the sesquicarbonate of ammonia collects as a transparent fibrous mass, which is extracted by taking the receiver to pieces, and purified by resubliming it at about 130° F., in iron vessels surmounted by leaden domes. The action of carbonate of lime upon hydrochlorate of ammonia would be expected to furnish the neutral carbonate ($2NH_3.H_2O.CO_2$), or $(NH_4)_2CO_3$, but this salt (even if produced) is decomposed by the heat employed in the process, with loss of ammonia and water, and formation of sesquicarbonate of ammonia—



$$6(NH_3.HCl) + 3(CaO.CO_2) = 4NH_3.2H_2O.3CO_2 + 2NH_3 + H_2O + 3CaCl_2.$$

When a mass of freshly prepared sesquicarbonate of ammonia is exposed to air, it evolves ammonia and carbonic acid, and becomes gradually converted into an opaque crumbly mass of bicarbonate of ammonia—



$$4NH_3.2H_2O.3CO_2 = 2NH_3 + CO_2 + 2(NH_3.H_2O.CO_2).$$

Water effects this decomposition more rapidly; if the powdered sesquicarbonate of ammonia be washed with a little water, bicarbonate of ammonia is left, and the solution contains the elements of neutral carbonate of ammonia ($2NH_3.H_2O.CO_2$), but this salt has not been obtained in the solid form. The sesquicarbonate dissolves in about three times its weight of cold water. Boiling water decomposes it, and the solution, on cooling, deposits large prismatic crystals of *bicarbonate of ammonia* ($NH_3.H_2O.CO_2$) which is much less soluble in water. This salt has been found in considerable quantity, forming crystalline masses in a bed of guano on the western coast of Patagonia. *Sal volatile* is an alcoholic solution of carbonate of ammonia obtained by distilling sal-ammoniac

with carbonate of potash and rectified spirit of wine, or by treating the sesquicarbonate of ammonia with hot spirit.

By dissolving sesquicarbonate of ammonia in strong solution of ammonia, and adding alcohol, prismatic crystals of the sesquicarbonate, of the formula $4NH_3.2H_2O.3CO_2.2Aq.$, may be obtained.

189. *Hydrochlorate of ammonia* ($NH_3.HCl$), or *chloride of ammonium* (NH_4Cl), also called *muriate of ammonia* and *sal-ammoniac.*—When dry ammonia gas is brought in contact with an equal volume of dry hydrochloric acid gas, it has been seen (p. 125) that they combine directly to produce the hydrochlorate of ammonia, the preparation of which on the large scale has been noticed at p. 120. It is also sometimes made by subliming a mixture of sulphate of ammonia with common salt—



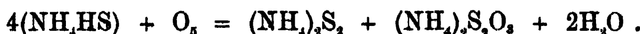
$$2NH_3.H_2O.SO_3 + 2NaCl = 2(NH_3.HCl) + Na_2O.SO_3.$$

Its commercial form is that of a very tough translucent fibrous mass, generally of the dome-like shape of the receivers, and often striped with brown, from the presence of a little iron. It has not the least smell of ammonia, and is very soluble in water, requiring about three parts of cold water, and little more than its own weight of boiling water. As the hot solution cools, it deposits beautiful fern-like crystallisations composed of minute cubes and octahedra. The liquefaction of sal-ammoniac in water lowers the temperature very considerably, which renders the salt very useful in freezing mixtures. A mixture of equal weights of sal-ammoniac and nitre, dissolved in its own weight of water, lowers the temperature of the latter from 50° F. to 10°. In this case partial decomposition takes place, resulting in the production of chloride of potassium and nitrate of ammonia, both of which absorb much heat whilst being dissolved by water. The solution of hydrochlorate of ammonia in water is slightly acid to blue litmus paper. When sal-ammoniac is heated, it passes off in vapour, at a temperature below redness, without previously fusing; the vapour forms thick white clouds in the air, and may be recondensed as a white crust upon a cold surface; but it cannot be sublimed without some loss, a portion being decomposed into hydrochloric acid, hydrogen, and nitrogen.

The specific gravity (weight of 1 vol.) of the vapour of sal-ammoniac is 13·3 times that of hydrogen, so that 53·5 parts, or one molecule, would appear to occupy 4 vols. instead of 2, but this may be explained by supposing a temporary *dissociation* of the hydrochloric acid and ammonia when the salt is converted into vapour, so that the observed specific gravity is really that of a mixture of equal volumes of these constituent gases. Some experimental evidence has been obtained in support of this view, for it has been found that free ammonia and hydrochloric acid may be separated by diffusion from the vapour obtained on heating hydrochlorate of ammonia. Moreover, the heat which becomes latent or is *absorbed* in vaporising the sal-ammoniac is almost exactly that which is *produced* by the combination of the hydrochloric acid and ammonia. When this salt is heated with metallic oxides, its hydrochloric acid often converts the oxide into a chloride which is either fusible or volatile, so that sal-ammoniac is often employed for cleansing the surfaces of metals previously to soldering them. Even those metallic oxides which are destitute of basic properties, such as antimonic and stannic acids, are convertible into chlorides by the action of sal-ammoniac at a high temperature.

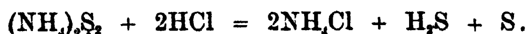
Hydrochlorate of ammonia is found in volcanic districts, and is present in very small quantity in sea-water.

190. *Hydrosulphate of ammonia* ($2NH_3.H_2S$), or *sulphide of ammonium* $(NH_4)_2S$, has been obtained in colourless crystals by mixing hydrosulphuric acid gas with twice its volume of ammonia gas in a vessel cooled by a mixture of ice and salt. It is a very unstable compound, decomposing at the ordinary temperature of the air into free ammonia and *bi-hydrosulphate of ammonia*, $NH_3.H_2S$, which may be obtained in very volatile colourless needles by passing equal volumes of its constituent gases into a vessel cooled in ice. When a solution of ammonia is saturated with hydrosulphuric acid gas, the ammonia is found to have combined with two molecules, forming a solution of the bi-hydrosulphate or *hydrosulphate of ammonium* (NH_4HS). The solution is colourless when freshly prepared, but it soon becomes yellow in contact with the air, from the formation of the *bisulphide of ammonium* $(NH_4)_2S_2$), hyposulphite of ammonia being formed at the same time—



$$4(NH_4HS) + O_5 = (NH_4)_2S_2 + (NH_4)_2S_2O_3 + 2H_2O .$$

Eventually, the solution deposits sulphur and becomes colourless, hyposulphite, sulphite, and sulphate of ammonia being formed. When the freshly prepared colourless solution of the bi-hydrosulphate of ammonia is mixed with an acid, the solution remains clear, hydrosulphuric acid being evolved with effervescence; $NH_3.H_2S + HCl = NH_3.HCl + H_2S$; but if the solution be yellow, a milky precipitate of sulphur is produced, from the decomposition of the bisulphide of ammonium—



$$(NH_4)_2S_2 + 2HCl = 2NH_4Cl + H_2S + S .$$

The fresh solution gives a black precipitate of sulphide of lead when solution of acetate of lead is added to it, but after it has been kept till it is of a dark yellow or red colour, it gives a red precipitate of the persulphide of lead. Solution of hydrosulphate of ammonia, prepared by mixing the bi-hydrosulphate with an equal volume of solution of ammonia, is largely employed in analytical chemistry. The solution has a very disagreeable odour.

Bisulphide of ammonium is obtained in deliquescent yellow crystals, when a mixture of ammonia gas with vapour of sulphur is passed through a red-hot porcelain tube. It is the chief constituent of *Boyle's fuming liquor*, a fetid yellow liquid obtained by distilling sal-ammoniac with sulphur and lime. The bisulphide of ammonium is sometimes deposited in yellow crystals from this liquid. By dissolving sulphur in the bisulphide of ammonium, orange-yellow prismatic crystals of *pentasulphide of ammonium* $(NH_4)_2S_5$ may be obtained. Even a *heptasulphide of ammonium* $(NH_4)_2S_7$ has been crystallised.

Compounds may be obtained in which the sulphide of ammonium $(NH_4)_2S$ plays the part of a sulphur-base towards the sulphides of arsenic, antimony, and other sulphur-acids.

It is scarcely possible to represent the constitution of the higher sulphides of ammonium except on the ammonium hypothesis.

The *hydrobromate of ammonia* ($NH_3.HBr$), or *bromide of ammonium* (NH_4Br), and the hydriodate of ammonia ($NH_3.HI$), or *iodide of ammonium* (NH_4I), are useful in photography. They are both colourless crystalline salts, but the iodide is very liable to become yellow or brown, from the separation of iodine, unless kept dry and in the dark. Both salts are extremely soluble in water.

191. LITHIUM (L = 7 parts by weight) is a comparatively rare metal, obtained chiefly from the minerals *lepidolite* (λεπίς, *a scale*) or *lithia-mica*, containing silicate of alumina with fluorides of potassium and lithium; *petalite* (πέταλον, *a leaf*), silicate of soda, lithia, and alumina, and *triphane* or *spodumene* (σποδός, *ashes*), which has a

similar composition. Its name (from λίθος, *a stone*) was bestowed in the belief that it existed only in the mineral kingdom, but recent investigation has detected it in minute proportion in the ashes of tobacco and other plants.

Metallic lithium is obtained by decomposing fused chloride of lithium by a galvanic current. It is remarkable as the lightest of the solid elements (sp. gr. 0·59). It bears a general resemblance to potassium and sodium, but is harder and less easily oxidised than those metals. It decomposes water rapidly at the ordinary temperature, but does not inflame upon it.

The alkali lithia (L_2O) powerfully corrodes platinum when heated upon it, and also differs from potash and soda by forming a sparingly soluble phosphate ($3L_2O.P_2O_5$) and carbonate ($L_2O.CO_2$). The compounds of lithium impart a red colour to the flame of the blowpipe (p. 260).

Carbonate of lithia is occasionally employed medicinally.

RUBIDIUM (Rb′ = 85 parts by weight) and CÆSIUM (Cs′ = 133 parts by weight) were discovered so lately as in 1860, by Bunsen and Kirchhoff, during the analysis of a certain spring water which contained these metals in so minute quantity (2 or 3 grs. in a ton) that they would certainly have escaped observation if the analysis had been conducted in the ordinary way. The discovery of these metals, as well as of two others (thallium and indium) to be mentioned hereafter, was the result of the application of the method of *spectrum analysis*, of which a brief description is here given, although the discussion of the optical principles upon which it depends would be misplaced in a chemical work.

192. *Spectrum analysis.*—It has been mentioned above that compounds of potassium, sodium, and lithium impart, respectively, lilac, yellow, and red colours to the blowpipe flame (or air-gas flame, see p. 103), or, in other words, that the highly heated vapours of the metals evolve luminous rays of these particular colours. When the quantity of the metal is extremely minute, and its peculiar luminous rays proportionally scanty, their colour may very easily escape notice, especially if two or three metals are present in the flame at the same time. But if the light emanating from the flame be collected by a lens (at A, fig. 237), and transmitted through a prism of flint glass, or through a hollow prism filled with bisulphide of carbon (B), all the rays of one colour will be refracted in a definite direction, so that the *spectrum*, or image of the flame, when thrown upon a screen, instead of exhibiting colours uniformly distributed like the flame itself, will show stripes or bands of the various coloured rays existing in the flame. Thus, when vapour of sodium is present in the flame, the whole of the yellow light emitted by it will be collected in the *spectrum* into a narrow yellow stripe of great intensity, and so extremely delicate is this test that it is scarcely possible to obtain a flame which does not exhibit this *sodium line*. The heated vapour of lithium emits a mixture of red with a few yellow rays, and accordingly, the spectrum of a flame containing lithium exhibits a very bright band of red light, and a comparatively dull band of yellow light, the red band being characteristic of lithium. The potassium flame emits a mixture of blue and red rays, so that its spectrum exhibits a distinct red band of a darker colour than the lithium band, and a feeble violet band. Instead of throwing the spectrum upon a screen, it

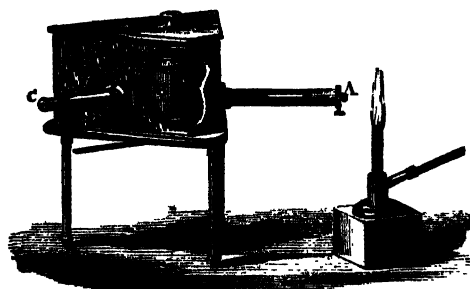
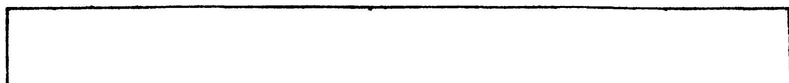


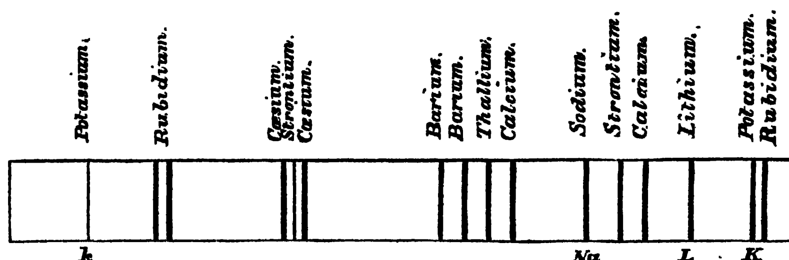
Fig. 237.—Spectroscope.

is generally passed through a telescope (C) to the eye of the observer, and the *spectroscope* so constructed has now taken its place among the apparatus indispensable to the analytical chemist. The prism B may be slowly moved round by a handle attached to a stage on which it rests, in order that the different parts of the spectrum may be successively brought into sight. By comparing the spectra of the flames containing vapours of the metals with a picture or map of the solar spectrum (fig. 238), the exact position of the various coloured bands may be noted, and thus, if several metals are present in the same flame, they may still be distinguished by the colours and positions of their bands. Thus, if a mixture of the chlorides of potassium, sodium, and lithium be taken upon a loop of platinum wire and held in the flame, the dull red line of potassium (K, fig. 238) is seen close to one end of the spectrum, at some distance from it the bright red band (L) of lithium; at about the same distance

Violet. Indigo. Blue. Green. Yellow. Orange. Red.



Spectrum furnished by solar light decomposed by a prism.



Coloured bands in the spectrum.

Fig. 238.

from this, the pale yellow lithium line; and close to this, the bright yellow band of sodium (Na); whilst near to the other end of the spectrum is the feeble violet band of potassium (*k*). The chlorides of the metals are most suitable for this experiment, on account of their easy conversion into vapour.

When examining, with the spectroscope, the alkaline chlorides extracted from the spring water above alluded to, Bunsen and Kirchhoff observed two red and two blue bands in the spectrum, which they could not ascribe to any known substance, and which they ultimately traced to the two new metals, rubidium (*rubidus, dark-red*) and cæsium (*cæsius, sky-blue*).

Rubidium has since been found in small quantity in other mineral waters, in lepidolite and in the ashes of many plants. This metal is closely related in properties to potassium, but is more easily fusible and convertible into vapour, and actually surpasses that metal in its attraction for oxygen, rubidium taking fire spontaneously in air. It burns on water with exactly the same flame as potassium. Its oxide, *rubidia* (Rb_2O), is a powerful alkali, like potash, and its salts are isomorphous with those of potash. The double chloride of platinum and potassium, however, is eight times as soluble in boiling water as the corresponding salt of rubidium, which is taken advantage of in separating these two allied metals.

Cæsium appears to be even more highly electropositive than rubidium, forming a

strong alkali, *cæsia* (Cs_2O), with oxygen, and salts which are isomorphous with those of potassium. Carbonate of cæsia, however, is soluble in alcohol, which does not dissolve the carbonates of potash and rubidia. Moreover, the bitartrate of cæsia is nine times as soluble in water as the bitartrate of rubidia.

Cæsium has been found in lepidolite; and the rare mineral *pollux* found in Elba, and resembling feldspar in composition, is said to contain a very large quantity of this metal.

193. *General review of the group of alkali-metals.*—Cæsium, rubidium. potassium, sodium, and lithium, constitute a group of elements conspicuous for their highly electropositive character, the powerfully alkaline nature of their oxides, and the general solubility of their salts. Their chemical characters and functions are directly opposite to those of the electronegative group containing fluorine, chlorine, bromine, and iodine, and, like those elements, they exhibit a gradation of properties. Thus, cæsium appears to be the most highly electropositive member, rubidium the next, then potassium and sodium, whilst lithium is the least electropositive; and just as iodine, the least electronegative of the halogens, possesses the highest atomic number, so cæsium, the least electronegative (or most electropositive) of the alkali-metals, has a higher atomic weight than any other member of this group, their atomic weights being represented by the numbers, cæsium, 133; rubidium, 85·3; potassium, 39; sodium, 23; lithium, 7. As in the case of the halogens, also, there is no reason to believe that the atomic weights of this group differ from their equivalent weights, so that they are all univalent elements. Just as chlorine is accepted as the representative of *chlorous radicals*, so potassium is commonly regarded as the type of *basylous radicals*, the term radical being applied to all substances, whether elementary or compound, which are capable of being transferred, like chlorine or potassium, from one compound to another without suffering decomposition.

Some of the physical properties of these elements exhibit a gradation in the same order as their atomic weights; thus rubidium fuses at 101° F., potassium at 144°·5, sodium at 207°·7, and lithium at 356°, so that, at ordinary temperatures, rubidium is the softest, and lithium the hardest of these metals.

In some of their salts a similar gradational relation is observed; the carbonates, for example, of cæsia, rubidia, and potassa, are highly deliquescent, absorbing water greedily from the air, whilst carbonate of soda is not deliquescent, and carbonate of lithia is sparingly soluble in water. The difficult solubility of the carbonate and phosphate of lithia constitutes the connecting link between this and the succeeding group of metals, the carbonates and phosphates of which are insoluble in water.

BARIUM.

Ba″ = 137 parts by weight.

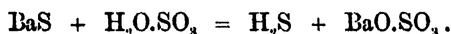
194. Barium, so named from the great weight of its compounds (βαρύς, *heavy*) is found in considerable abundance in the north of England, in two minerals known as *Witherite* (carbonate of baryta, $BaO.CO_2$) and *heavy spar* (sulphate of baryta, $BaO.SO_3$). Witherite is found in large masses in the lead mines at Alston Moor, and at Anglesark in Lancashire. It is said to be used for poisoning rats, and was originally mistaken, on account of its great weight, for an ore of lead.

The metal itself is obtained by decomposing fused chloride of barium by the galvanic current. It is a pale yellow, fusible, malleable metal of

sp. gr. about 4, which is easily oxidised by air, and rapidly decomposes water at common temperatures.

Such compounds of baryta as are used in the arts are chiefly prepared from heavy spar or sulphate of baryta, which is remarkable for its insolubility in water and acids. In order to prepare other compounds of baryta from this refractory mineral, it is ground to powder and strongly heated in contact with charcoal or some other carbonaceous substance, which removes the oxygen from the mineral in the form of carbonic oxide, and converts it into *sulphide of barium;* $BaO.SO_3 + C_4 = 4CO + BaS$. This latter compound, being soluble in water, can be readily converted into other barytic compounds.

The artificial *sulphate of baryta* which is used by painters, instead of white lead, under the name of *permanent white*, and is employed for glazing cards, is prepared by mixing the solution of sulphide of barium with dilute sulphuric acid, when the sulphate of baryta separates as a white precipitate, which is collected, washed, and dried—



$$BaS + H_2O.SO_3 = H_2S + BaO.SO_3.$$

The artificial *carbonate of baryta*, which is used in the manufacture of some kinds of glass, is prepared by passing carbonic acid gas through a solution of sulphide of barium, when the carbonate of baryta is precipitated; $BaS + H_2O + CO_2 = H_2S + BaO.CO_2$.

In preparing compounds of barium from heavy spar on the small scale, it is better to convert the sulphate of baryta into carbonate of baryta. 50 grs. of the finely powdered sulphate are mixed with 100 grs. of dried carbonate of soda, 600 grs. of powdered nitre, and 100 grs. of very finely powdered charcoal. The mixture is placed in a heap upon a brick or iron plate, and kindled with a match, when the heat evolved by the combustion of the charcoal in the oxygen of the nitre, fuses the sulphate of baryta with the carbonate of soda, when they are decomposed into carbonate of baryta and sulphate of soda—



$$BaO.SO_3 + Na_2O.CO_2 = Na_2O.SO_3 + BaO.CO_2.$$

The fused mass is thrown into boiling water, which dissolves the sulphate of soda and leaves the carbonate of baryta. The latter may be allowed to settle, and washed several times, by decantation, with distilled water, until the washings no longer yield a precipitate with chloride of barium, showing that the whole of the sulphate of soda has been washed away, and pure carbonate of baryta remains.

Nitrate of baryta, $BaO.N_2O_5$ or $Ba(NO_3)_2$, is obtained by dissolving carbonate of baryta in diluted nitric acid, and evaporating the solution, when octahedral crystals of the nitrate are deposited. It is an ingredient in some kinds of blasting powder used by miners. If nitrate of baryta be heated in a porcelain crucible, it fuses and is decomposed, leaving a grey porous mass of *baryta;* $BaO.N_2O_5 = BaO + 2NO_2 + O$.

Hydrate of baryta may be procured by adding 4 oz. of the powdered nitrate of baryta to 12 oz. of a boiling solution of hydrate of soda, of sp. gr. 1·13 (prepared by dissolving 3 oz. of commercial hydrate of soda in 20 measured ounces of water); the solution becomes turbid from the separation of carbonate of baryta produced from the carbonate of soda in the hydrate; it is boiling for some minutes and then filtered; on partial cooling, some crystals of undecomposed nitrate of baryta are deposited, and if the clear liquid be poured off into another vessel and stirred, it deposits abundant crystals of hydrate of baryta, having the composition $BaO.H_2O.8Aq.$; these effloresce and become opaque when exposed to air, becoming $BaO.H_2O.Aq.$; when heated to redness, they become pure hydrate of baryta, $BaO.H_2O$, which fuses but is not decomposed when

further heated. The hydrate of baryta is moderately soluble in water, the solution being strongly alkaline, and absorbing carbonic acid from the air, depositing carbonate of baryta.

When baryta is heated in a tube through which oxygen or air is passed, it absorbs the oxygen and is converted into binoxide of barium (BaO_2), which is employed for the preparation of peroxide of hydrogen (see p. 51).

Chloride of barium, which is the barium compound most commonly employed in the laboratory, may be obtained by dissolving the carbonate of baryta in diluted hydrochloric acid, and evaporating the solution; on cooling, the chloride is deposited in tabular crystals, $BaCl_2.2Aq$.

On the large scale it is generally manufactured by fusing heavy spar (sulphate of baryta) with chloride of calcium (the residue from the preparation of ammonia, see p. 120), in a reverberatory furnace—



$$BaO.SO + CaCl_2 = CaO.SO_3 + BaCl_2 .$$

The mass is rapidly extracted with hot water, which leaves the sulphate of lime undissolved, and the clear solution of chloride of barium is decanted and evaporated. If the sulphate of lime and chloride of barium were allowed to remain long together in contact with the water, sulphate of baryta and chloride of calcium would be reproduced.

Chlorate of baryta ($BaO.Cl_2O_5$, or $Ba\ (ClO_3)_2$) is employed in the manufacture of fireworks, being prepared for that purpose by dissolving the artificial carbonate of baryta in solution of chloric acid; it forms beautiful shining tabular crystals. When mixed with combustible substances, such as charcoal and sulphur, it imparts a brilliant green colour to the flame of the burning mixture (see p. 164).

All the soluble salts of barium are very poisonous.

STRONTIUM.

$Sr'' = 87{\cdot}5$ parts by weight.

195. Strontium is less abundant than barium, and occurs in nature in similar forms of combination. *Strontianite*, the *carbonate of strontia* ($SrO.CO_2$), was first discovered in the lead mines of Strontian in Argyleshire, and has since been found in small quantity in some mineral waters.

Celestine (so called from the blue tint of many specimens) is the *sulphate of strontia* ($SrO.SO_3$), and is found in beautiful crystals associated with the native sulphur in Sicily. It is also met with in this country, and is the source from which the *nitrate of strontia* employed in firework compositions is derived. The sulphate of strontia resembles that of baryta with respect to its insolubility, and is converted into the soluble *sulphide of strontium* (SrS) by calcination with carbonaceous matter. The solution of sulphide of strontium so obtained is decomposed by nitric acid, and the nitrate of strontia crystallised from the solution. This salt forms prismatic crystals which have the formula $SrO.N_2O_5.5Aq$. It has the property of imparting a magnificent crimson colour to flames, and is hence largely used for the preparation of red theatrical fire. (See p. 164.) The other compounds of strontium possess too little practical importance, and too nearly resemble those of barium, to require particular description here. No peroxide of strontium, however, has been obtained.

The metal itself is prepared in a similar manner to metallic barium, which it much resembles, though it is lighter (sp. gr. 2·54) and less fusible. It burns, when heated in air, with a crimson flame.

CALCIUM.

$Ca'' = 40$ parts by weight.

196. No other metal is so largely employed in a state of combination as calcium, for its oxide, lime (CaO), occupies among bases much the same position as that which sulphuric acid holds among the acids, and is used, directly or indirectly, in most of the arts and manufactures.

Like barium and strontium, it is found, though far more abundantly than these, in the mineral kingdom, in the forms of carbonate and sulphate, but it also occurs in large quantity as fluoride of calcium (p. 181), and less frequently in the form of phosphate of lime (p. 223). Calcium, moreover, is found in all animals and vegetables, and its presence in their food, in one form or other, is an essential condition of their existence.

Metallic calcium may be obtained by decomposing fused iodide of calcium with metallic sodium. It has a light golden-yellow colour, is harder than lead, and very malleable; it oxidises slowly in air at the ordinary temperature, but when heated to redness, it fuses and burns with a very brilliant white light, being converted into lime (*calx*). It decomposes water at the ordinary temperature. It is lighter than barium and strontium, its specific gravity being 1·58.

Carbonate of Lime ($CaO.CO_2$ or $CaCO_3$), from which all the manufactured compounds of lime are derived, constitutes the different varieties of limestone which are met with in such abundance.

Limestones and *chalk* are simply carbonate of lime in an amorphous or uncrystallised state. The *oolite* limestone, of which the Bath and Portland building-stones are composed, is so called from its resemblance to the roe of a fish (ὠόν, an egg. *Marble*, in its different varieties, is an assemblage of minute crystalline grains of carbonate of lime, sometimes variegated by the presence of oxides of iron and manganese, or of bituminous matter. This last constituent gives the colour to black marble. Carbonate of lime is also found in large transparent rhombohedral crystals, which are known to mineralogists as *calcareous spar*, *calc spar*, or *Iceland spar*. When the crystals have the form of a six-sided prism, the mineral is termed *Arragonite*. The attention of the crystallographer has long been directed to these two crystalline forms of carbonate of lime, on account of the circumstance, that if a prism of arragonite be heated, it breaks up into a number of minute rhombohedra of calc spar.

Carbonate of lime is a chief constituent of the shells of fishes and of egg shells, so that, except phosphate of lime, no mineral compound has so large a share in the composition of animal frames. *Corals* also consist chiefly of carbonate of lime derived from the skeletons of innumerable minute insects. The mineral *gaylussite* is a double carbonate of lime and soda ($CaO.CO_2$, $Na_2O.CO_2.5Aq.$), and is scarcely affected by water unless previously heated, when water dissolves out the carbonate of soda. *Baryto-calcite* is a double carbonate of baryta and lime ($BaO.CO_2$, $CaO.CO_2$).

Lime (CaO).—The process by which lime is obtained from the carbonate has been already alluded to under the name of lime-burning. In order that the carbonic acid may be completely expelled from the carbonate of lime, it is necessary that the products of combustion of the fuel should be allowed to pass over the limestone, since although a very intense heat is insufficient to decompose carbonate of lime when shut up in a crucible, the decomposition is easily effected if the carbonate be

heated in a current of atmospheric air or of any other gas, especially if aqueous vapour be present, as is the case in the products of combustion of the fuel.

Accordingly, a kiln is commonly employed of the form of an inverted cone of brickwork (fig. 239), and into this the limestone and fuel are thrown in alternate layers. The former losing its carbonic acid before it reaches the bottom of the furnace, is raked out in the form of *burnt* or *quick* lime (CaO), whilst its place is supplied by a fresh layer of limestone thrown in at the top of the kiln. Fig. 240 represents another form

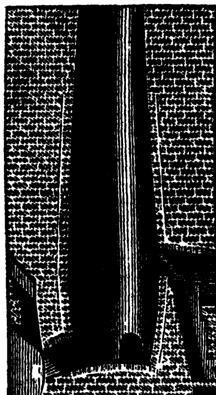


Fig. 239.—Lime.



Fig. 240.—Lime-kiln.

of kiln, in which the limestone is supported upon an arch built with large lumps of the stone above the fire, which is kept burning for about three days and nights, until the whole of the limestone is decomposed.

The usual test of the quality of the lime thus obtained consists in sprinkling it with water, with which it should eagerly combine, evolving much heat, swelling greatly, and crumbling to a light white powder of *hydrate of lime* (*slaked lime*). Lime which behaves in this manner is termed *fat lime*; whereas, if it be found to slake feebly, it is pronounced a *poor lime*, and is known to contain considerable quantities of foreign substances, such as silica, alumina, magnesia, &c. Lime is said to be *overburnt* when it contains hard cinder-like masses of silicate of lime, formed by the combination of the silica, which is generally found in limestone, with a portion of the lime, under the influence of excessive heat in the kiln.

The hydrate of lime is about twice as soluble in cold as it is in hot water, so that *lime-water* should always be made by shaking slaked lime with cold distilled water, which dissolves about 1-700th of its weight; the solution is allowed to settle in a closed bottle, for it absorbs carbonic acid rapidly from the air. Crystals of hydrate of lime have been obtained by evaporating lime-water *in vacuo*.

Sulphate of Lime in combination with water ($CaO.SO_3.H_2O.Aq.$) is met with in nature, both in the form of transparent prisms of *selenite*, and in opaque and semi-opaque masses known as *alabaster* and *gypsum*. It is this latter form which yields *plaster of Paris*, for when heated to between 300° and 400° F., it loses its water, and if the mass be then powdered, and again mixed with water, the powder recombines with it

to form a mass of hydrated sulphate of lime, the hardness of which nearly equals that of the original gypsum.

In the preparation of plaster of Paris, a number of large lumps of gypsum are built up into a series of arches, upon which the rest of the gypsum is supported; under these arches the fuel is burnt, and its flame is allowed to traverse the gypsum, care being taken that the temperature does not rise too high, or the gypsum is *overburnt* and does not exhibit the property of recombining with water. When the operation is supposed to be completed, the lumps are carefully sorted, and those which appear to have been properly calcined are ground to a very fine powder. When this powder is mixed with water to a cream, and poured into a mould, the minute particles of anhydrous sulphate of lime ($CaO.SO_3$) combine with 2 molecules of water to reproduce the original gypsum ($CaO.SO_3.H_2O.Aq.$), and this act of combination is attended with a slight expansion which forces the plaster into the finest lines of the mould.

Stucco consists of plaster of Paris (occasionally coloured) mixed with a solution of size; certain cements used for building purposes (Keene's and Keating's cements) are prepared from burnt gypsum, which has been soaked in a solution of alum and again burnt; and although the plaster thus obtained takes much longer to set than the ordinary kind, it is much harder, and therefore takes a good polish.

Plaster of Paris is much damaged by long exposure to moist air, from which it regains a portion of its water, and its property of setting is so far diminished.

Precipitated sulphate of lime is used by paper-makers under the name of *pearl hardener.*

Chloride of calcium ($CaCl_2$) has been mentioned as the residue left in the preparation of ammonia. The pure salt may be obtained by dissolving pure carbonate of lime (white marble) in hydrochloric acid, and evaporating the solution, when prismatic crystals of the composition $CaCl_2.6Aq.$ are obtained. When these are heated they melt, and at about 390° F. are converted into a white porous mass of $CaCl_2.2Aq.$, which is much used for drying gases. At a higher temperature, fused chloride of calcium, free from water, is left; this is very useful for removing water from some liquids. A saturated solution of chloride of calcium boils at 355° F., and is sometimes used as a convenient bath for obtaining a temperature above the boiling point of water.

When hydrate of lime is boiled with a strong solution of chloride of calcium, it is dissolved, and the filtered solution deposits prismatic crystals of *oxychloride of calcium*, $CaCl_2.3CaO.15Aq.$, which are decomposed by pure water.

MAGNESIUM.

$Mg'' = 24{\cdot}3$ parts by weight.

197. Magnesium is found, like calcium, though less abundantly, in each of the three natural kingdoms. Among minerals containing this metal, those with which we are most familiar are certain combinations of silica and magnesia (silicates of magnesia) known by the names of *talc*, *steatite* or *French chalk*, *asbestos*, and *meerschaum*, which always contains water. *Magnesite* is a carbonate of magnesia. Most of the minerals containing magnesium have a remarkably soapy feel. The compounds of

magnesium, which are employed in medicine, are derived either from the mineral *dolomite* or *magnesian limestone*, which contains the carbonate of magnesia and carbonate of lime, or from the sulphate of magnesia, which is obtained from sea-water and from the waters of many mineral springs.

Metallic magnesium has acquired some importance during the last few years as a source of light. When the extremity of a wire of this metal is heated in a flame, it takes fire, and burns with a dazzling white light, becoming converted into magnesia (MgO). If the burning wire be plunged into a bottle of oxygen, the combustion is still more brilliant. The light emitted by burning magnesium is capable of inducing chemical changes similar to those caused by sun-light, a circumstance turned to advantage for the production of photographic pictures by night. Attempts have been made to introduce magnesium as an illuminating agent for general purposes, but the large quantity of solid magnesia produced in its combustion forms a very serious obstacle to its use. The metal is extracted from the chloride of magnesium (see p. 115) by fusing it with sodium, using chloride of sodium and fluoride of calcium to promote the fusibility of the mass.

On a small scale, magnesium may be prepared by mixing 900 grs. of chloride of magnesium with 150 grs. of fluoride of calcium, 150 of fused chloride of sodium, and 150 of sodium cut into slices (see p. 115). The mixture is thrown into a red-hot earthen crucible, which is then covered and again heated. When the action appears to have terminated, the fused mass is stirred with an iron rod to promote the union of the globules of magnesium. It is then poured upon an iron tray, allowed to solidify, broken up, and the globules of magnesium separated from the slag; they may be collected into one globule by throwing them into a melted mixture of chlorides of magnesium and sodium and fluoride of calcium.

In most of its physical and chemical characters magnesium resembles zinc, though its colour more nearly approaches that of silver; in ductility and malleability it also surpasses zinc. It is nearly as light, however, as calcium, its specific gravity being 1·74. It fuses below a red heat, and may be distilled like zinc. Cold water has scarcely any action upon magnesium; even when boiled it oxidises the metal very slowly. In the presence of acids, however, it is rapidly oxidised by water. Solution of hydrochlorate of ammonia also dissolves it, owing to the tendency of the magnesium salts to form double salts with those of ammonia—



$$4(NH_3.HCl) + Mg = 2(NH_3.HCl).MgCl_2 + H_2 + 2NH_3.$$

Magnesium is one of the few elements which unite directly with nitrogen at a high temperature. The *nitride of magnesium*, N_2Mg_3, has been obtained in transparent crystals, and is evidently composed after the type $2NH_3$, so that it is not surprising that the action of water upon it gives rise to magnesia and ammonia, $N_2Mg_3 + 6HO = 2NH_3 + 3MgO$.

The *sulphate of magnesia*, so well known as Epsom salts, is sometimes prepared by calcining dolomite to expel the carbonic acid, washing the residual mixture of lime and magnesia with water to remove part of the lime, and treating it with sulphuric acid which converts the lime and magnesia into sulphates; and since the sulphate of lime is almost insoluble in water, it is readily separated from the sulphate of magnesia which passes into the solution, and is obtained by evaporation in prismatic crystals having the composition $MgO.SO_3.H_2O.6Aq$. The prepara-

tion of Epsom salts from sea-water has already been alluded to (p. 262). In some parts of Spain, sulphate of magnesia is found in large quantities (like nitre in hot climates) as an efflorescence upon the surface of the soil. This sulphate of magnesia, as well as that contained in well-waters, appears to have been produced by the action of sulphate of lime, originally present in the water, upon magnesian limestone rocks; $MgO.CO_2 + CaO.SO_3 = MgO.SO_3 + CaO.CO_2$.

The water of constitution in the sulphate of magnesia may be displaced by the sulphate of an alkali without alteration in its crystalline form; a double sulphate of magnesia and potash ($MgO.SO_3, K_2O.SO_3.6Aq.$), and a similar salt of ammonia ($MgO.SO_3, 2NH_3.H_2O.SO_3.6Aq.$) may be thus obtained. The mineral *polyhalite* (πολὺς, *many*, ἅλς, *salt*) is a remarkable salt, containing $MgO.SO_3, K_2O.SO_3, 2(CaO.SO_3), 2H_2O$.* Water decomposes it into its constituent salts.

The preparation commonly used in medicine under the name of magnesia, is really a *basic carbonate of magnesia*, or a compound of carbonate of magnesia with hydrate of magnesia and water in the proportions expressed by the formula, $3(MgO.CO_2).MgO.H_2O.3Aq$. It is obtained by mixing boiling solutions of sulphate of magnesia and carbonate of soda, when one-fourth of the carbonic acid is expelled in the state of gas; the white precipitate is thrown upon a cloth strainer, well washed, and dried in rectangular moulds.

Another process for preparing carbonate of magnesia consists in heating magnesian limestone to low redness, so as to decompose the carbonate of magnesia which it contains, and exposing it, under pressure, to the action of water and carbonic acid, which dissolves the magnesia and leaves the carbonate of lime. On boiling the solution, to expel the excess of carbonic acid, the carbonate of magnesia is precipitated.

By moderately heating the carbonate of magnesia, its water and carbonic acid are expelled, and pure or *calcined magnesia* (MgO) is left, which is very slightly soluble in water and feebly alkaline.

The mineral *periclase* consists of magnesia in a crystallised form. Magnesia combines with water to form a hydrate ($MgO.H_2O$), but not with evolution of heat, as in the cases of baryta, strontia, and lime. Crystallised hydrate of magnesia constitutes the mineral *brucite*. Magnesia, like lime, is remarkable for its infusibility.

It has recently been noticed that calcined magnesia, when mixed with water, solidifies after a time into a very hard compact mass of hydrate of magnesia ($MgO.H_2O$), and may serve, like plaster of Paris, for taking casts. Dolomite calcined below redness also sets to a very hard mass with water.

The *phosphate of magnesia* ($3MgO.P_2O_5$) enters into the composition of bones, and the *phosphate of magnesia and ammonia* ($2MgO.2NH_3.H_2O.P_2O_5$), or *triple phosphate*, is found in calculi and in the minerals *guanite* and *struvite*.

Borate of magnesia composes the mineral *boracite*; *hydroboracite* is a hydrated borate of lime and magnesia.

Serpentine and *olivine* are silicates of magnesia and protoxide of iron. Some of the varieties of serpentine are employed for preparing the compounds of magnesia, for they are easily decomposed by acids with separation of silica.

Pearl-spar is a crystallised carbonate of lime and magnesia.

* Polyhalite and *kieserite* $MgO.SO_3, H_2O$ are found in the salt-beds of Stassfurth.

Chloride of magnesium is important as the source of metallic magnesium. It is easily obtained in solution by neutralising hydrochloric acid with magnesia or its carbonate, but if this solution be evaporated in order to obtain the dry chloride, a considerable quantity of the salt is decomposed by the water at the close of the evaporation, leaving much magnesia mixed with the chloride ($MgCl_2 + H_2O = 2HCl + MgO$). This decomposition may be prevented by mixing the solution with three parts of hydrochlorate of ammonia for every part of magnesia, when a double salt $MgCl_2.NH_3.HCl$ is formed, which may be evaporated to dryness without decomposition, and leaves fused chloride of magnesium when further heated, the hydrochlorate of ammonia being volatilised. The chloride of magnesium absorbs moisture very rapidly from the air, and is very soluble in water. Like all the soluble salts of magnesium, it has a decidedly bitter taste. When magnesia is moistened with a strong solution of chloride of magnesium, it sets into a hard mass like plaster of Paris, apparently from the formation of an oxychloride $MgO.MgCl_2$. It may be mixed with several times its weight of sand, and will bind it firmly together.

198. *General review of the metals of the alkaline earths.*—Barium, strontium, calcium, and magnesium form a highly interesting natural group of metals related to each other in a most remarkable manner. They exhibit a marked gradation in their attraction for oxygen; barium is more readily tarnished or oxidised, even in dry air, than strontium, and strontium more readily than calcium; whilst magnesium is not at all affected by dry air, and is comparatively slowly tarnished even in moist air. Again, the three first metals decompose water at the ordinary temperature, combining with its oxygen and liberating the hydrogen, but magnesium requires the aid of heat to effect this decomposition. The oxides of the metals exhibit a similar gradation in properties; baryta, strontia, and lime combine with water very energetically with great evolution of heat, whilst in the case of magnesia no rise of temperature is observed; the hydrate of baryta does not lose its water, however strongly it may be heated, whereas the hydrates of strontia and lime are decomposed at a red heat, and hydrate of magnesia even at a lower temperature. Then hydrate of baryta and hydrate of strontia are far more soluble in water than hydrate of lime (which requires about 700 parts of water to dissolve it), and all these three exhibit a very decided alkaline reaction which entitles them to the name of *alkaline earths;* but hydrate of magnesia requires about 3000 parts of water to dissolve it, and is so feebly alkaline, that it might even be fairly classed among the *earths proper.*

Among the other compounds of these metals, the sulphates may be named as presenting a gradation of a similar description; for sulphate of baryta may be said to be insoluble in water, sulphate of strontia dissolves to a very slight extent, sulphate of lime is rather more soluble, and the sulphate of magnesia is very readily dissolved by water. It will be seen hereafter that the sulphates of the earths proper are remarkable for their solubility in water, so that, in this respect also, magnesia appears to stand on the border line between the two classes.

The manner in which these metals are associated in nature is also not without its significance; for if two of them are found in the same mineral, they will usually be those which stand next to each other in the group; thus carbonate of strontia is found together with carbonate

of baryta in witherite, whilst carbonate of lime is associated with the sulphate of strontia in celestine. Again, carbonate of strontia is often found with carbonate of lime in arragonite, and the carbonate of magnesia occurs with carbonate of lime in dolomite.

199. *Equivalent and atomic weights of barium, strontium, calcium, and magnesium.*—The analysis of chloride of barium has proved it to contain 68·5 parts by weight of barium, combined with 1 eq. (35·5 parts) of chlorine; whence the equivalent of barium is accepted as 68·5. In a similar manner, that of strontium has been fixed at 43·8, that of calcium at 20, and that of magnesium at 12; so that here, as in the group of alkali-metals, the equivalent numbers decrease with the diminution of the electropositive character in the metals.

Relation between specific heats and equivalent weights. Atomic heats.—Since the specific volumes of the vapours of these metals have not been ascertained, recourse is had to their specific heats in order to ascertain their atomic weights. It will be remembered that the specific heat of a substance is the quantity of heat required to raise it 1° in temperature, as compared with the quantity of heat required to raise an equal weight of water 1°; or, more concisely, the quantity of heat required to raise one part by weight of the substance 1° (referred to water as the unit).

Thus, the specific heats of potassium, sodium, and lithium are, respectively, 0·1696, 0·2934, and 0·9408; these numbers representing the relative quantities of heat required to raise one part by weight of each of these metals 1° in temperature, supposing that an equal weight of water would be raised 1° by a quantity of heat expressed by *one*. No simple relation can be traced between these numbers, but if the quantities of heat be calculated which are required to raise *equivalent* weights of these elements 1°, the case will be different.

If 0·1696 be the quantity of heat required to raise one part by weight of potassium 1°; 0·1696 × 39, or 6·61, will represent the quantity of heat required to raise 39 parts (1 eq.) of potassium 1°. In the same way, 0·2934 × 23, or 6·75, is the quantity of heat required to raise 23 parts (1 eq.) of sodium 1°; and 0·9408 × 7, or 6·59, is the quantity required to raise 7 parts (1 eq.) of lithium 1°. Allowing for experimental error in the determination of the specific heats, these numbers, 6·61, 6·75, and 6·59, may be regarded as representing the same quantities of heat. Since the atomic weights of potassium, sodium, and lithium are expressed by the same numbers as their equivalent weights (see p. 274), the numbers, 6·61, 6·75, and 6·59, would represent the *atomic heats* of these metals, that is, the relative quantities of heat required to raise an atom of each 1° in temperature.

The atomic heat, therefore, which is common to these three metals, may be represented by the mean of the three numbers, or 6·65.

The experiments which have been made to determine the specific heats of those elements which can be obtained in a similar physical condition, lend strong support to the belief that the atomic heats of all elements belonging to the same group are identical, and even hold out a prospect of the identity of the atomic heats of a great majority of the elementary bodies.

A similar relation has been observed between the atomic heats of compound bodies belonging to the same group; thus, if the specific heats of

the chlorides of potassium, sodium, and lithium be multiplied by the atomic weights of those chlorides, the product in each case will approach very nearly to the number 12·69. If these chlorides be allowed to contain one atom of each of their constituents, and it be supposed that the atomic heats of these constituents are identical, the half of this number (or 6·34) should represent the atomic heat of the alkali-metals, and, in fact, it does nearly coincide with that number (6·65).

The specific heats of barium, strontium, and calcium have not been determined, and therefore their atomic heats cannot be directly ascertained. The specific heat of magnesium, however, is 0·2499, and if the atomic weight of this metal were identical with its equivalent (12), its atomic heat would be represented by the number 3; but if the atomic weight be regarded as double the equivalent, or 24, the atomic heat will be (0·2499 × 24) 6, a number more nearly approaching to the atomic heats of the alkali-metals. This is one reason for supposing that the atomic weight of magnesium is really represented by 24.

The specific heats of the chlorides of barium, strontium, calcium, and magnesium have been ascertained to be represented by the numbers 0·0900, 0·1180, 0·1686, and 0·1970, respectively. Now, if the atomic weights of these metals be regarded as identical with their equivalent weights, the atomic heats of the chlorides, obtained by multiplying their atomic weights into their specific heats, would be expressed by the mean number 9·36, and if this be divided by 2 (the presumed number of atoms in each chloride), it would give 4·68 for the atomic heat of each of the elements of the compound, a number which exhibits no simple relation to the atomic heat of magnesium, or to those of the alkali-metals. If it be supposed, however, that the atom of barium, strontium, calcium, or magnesium really represents two equivalents, so that each chloride contains three elementary atoms (two of chlorine and one of metal), the atomic weight of each of the chlorides would be doubled, and, consequently, the atomic heat would be twice that given above, or 18·72. Dividing this by 3, the presumed number of atoms in the chloride, we obtain the number 6·24 for the atomic heat of each of the elements, which agrees very well with that directly obtained for magnesium and the alkali-metals.

The metals barium, strontium, calcium, and magnesium, therefore, are generally regarded as bi-equivalent or diatomic elements, one atom of each occupying the place of two atoms of hydrogen.

ALUMINUM.

Al''' = 27·5 parts by weight.

200. Aluminum is the representative of the class of metals usually styled *metals of the earths proper*, and including also glucinum, thorinum, yttrium, zirconium, erbium, terbium, cerium, lanthanium, and didymium, but of these, aluminum is the only metal having any claim to our attention on the ground of its practical importance.

Aluminum is distinguished among metals, as silicon is among non-metallic bodies, for its immense abundance in the solid mineral portion of the earth, to which, indeed, it is almost entirely confined, for it is present in vegetables and animals in so small quantity that it can scarcely be regarded as forming one of their necessary components.

One of the oldest rocks, which appear to have originally formed the basis of the solid structure of the globe, is that known as *granite*. This mineral, which derives its name from its conspicuous *granular* structure, is a mixture, in variable proportions, of quartz, feldspar, and mica, tinged of various colours by the presence of small quantities of the oxides of iron and manganese.

Quartz, which forms the translucent or transparent grains in the granite, consists simply of silicic acid; *feldspar*, the dull cream-coloured opaque part, is a combination of that acid with alumina and potash, and is generally spoken of as a double silicate of alumina and potash, its composition being represented by the formula ($K_2O.3SiO_2,Al_2O_3.3SiO_2$)

Mica, so named from the *glittering* scales which it forms in the granite, is also a double silicate of alumina and potash, but the alumina is very frequently displaced by sesquioxide of iron, and the potash by magnesia.

By the long-continued action of air and water, the granite rock is gradually crumbled down or disintegrated, an effect which must be ascribed to a concurrence of mechanical and chemical causes. Mechanically, the rock is continually worn down by variations of temperature, by the congelation of water within its minute pores, the rock being gradually split by the expansion attendant upon such congelation. Chemically, the action of water containing carbonic acid would tend to remove the potash from the feldspar and mica in the form of carbonate of potash, whilst the silicate of alumina and the quartz would subsequently be separated by the action of water; the former, being so much lighter, would be soon washed away from the heavy quartz, and, when again deposited, would constitute *clay*.

Although clay, therefore, always consists mainly of silicate of alumina, it generally contains some uncombined silicic acid, together with variable quantities of lime, of oxide of iron, &c., which give rise to the numerous varieties of clay.

Composition of Clay.

	Chinese Kaolin.	Fire-clay. (Stourbridge).	Pipe-clay.
Silica	50·5	64·1	53·7
Alumina	33·7	23·1	32·0
Water	11·2	10·0	12·1
Oxide of iron	1·8	1·8	1·4
Lime	...	...	0·4
Magnesia	0·8	0·9	
Potash, Soda	1·9		
	99·9	99·9	99·6

The silicate of alumina also constitutes the chief portion of several other very important mineral substances, among which may be mentioned *slate*, *fuller's earth*, and *pumice-stone*. *Marl* is clay containing a considerable quantity of carbonate of lime. *Loam* is also an impure variety of clay. The different varieties of *ochre*, as well as *umber* and *sienna*, are simply clays coloured by the oxides of iron and manganese.

ALUM, which is the chief compound of aluminum employed in the arts, is always obtained either from clay or slate, but there are several processes by which it may be manufactured.

The simplest process is that in which pipe-clay, or some other clay containing very little iron, is calcined, ground to powder, and heated on the hearth of a reverberatory furnace with half its weight of sulphuric acid, until it becomes a stiff paste, which is then exposed to air for several weeks. During this time the alumina of the clay enters into combination with the sulphuric acid to form sulphate of alumina, which may be obtained by washing the mass with water, when the sulphate of alumina dissolves, and the undissolved silicic acid (still retaining a portion of the alumina) is left. When the solution containing the sulphate of alumina is evaporated to a syrupy consistence and allowed to cool, it solidifies into a white crystalline mass, which is used by dyers under the erroneous name of *concentrated alum*, or *cake-alum*, and contains about 47·5 per cent. of the dry salt. The sulphate of alumina can be obtained in crystals containing $Al_2O_3.3SO_3.18Aq.$, but there is considerable difficulty in obtaining these crystals on account of the extreme solubility of the salt. It is on account of this circumstance that the sulphate of alumina is usually converted into alum, which admits of very easy crystallisation and purification. In order to transform the sulphate of alumina into alum, its solution is mixed with sulphate of potash, when, by suitable evaporation, beautiful octahedral crystals are obtained, having the composition $Al_2O_3.3SO_3,K_2O.SO_3.24Aq.$

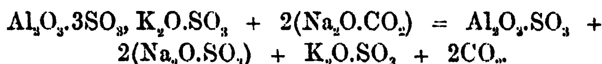
Alum is more commonly prepared from the mineral termed *alum-shale*, which contains silicate of alumina, together with a considerable quantity of finely divided iron pyrites and some bituminous matter. This shale is coarsely broken up, and built into long pyramidal heaps, together with alternate layers of coal, unless the shale should happen to contain a sufficient amount of bitumen. These heaps are set fire to in several places, and are partly smothered with spent ore in order to prevent too great a rise of temperature. During this slow roasting of the heap, the iron pyrites (FeS_2) loses half its sulphur, which is converted by burning into sulphurous acid (SO_2), and this, in contact with the porous shale and the atmospheric oxygen, becomes converted into sulphuric acid (p. 202). This latter acid combines with the alumina to produce sulphate of alumina. The roasted heap is then allowed to remain for some months exposed to the air, and moistened from time to time, in order to promote the absorption of oxygen by the sulphide of iron (FeS), and its conversion into sulphate of iron ($FeO.SO_3$). The heap is afterwards lixiviated with water, which dissolves out the sulphates of alumina and iron, together with some sulphate of magnesia, which has also been formed in the process. When this *crude alum liquor* is evaporated to a certain extent, a large quantity of sulphate of iron (green vitriol) crystallises out, and the liquid from which these crystals have separated is then mixed with so much solution of chloride of potassium as a preliminary experiment has shown to be necessary to yield the largest amount of alum. The chloride of potassium is obtained as soap-boiler's waste, and as the refuse from saltpetre refineries and glass-houses. The sulphate of iron still left in the solution is decomposed by the chloride of potassium, yielding chloride of iron and sulphate of potash, which combines with the sulphate of alumina to form alum. If there be much sulphate of magnesia in the liquor, it is subsequently obtained in crystals and sent into the market.

Where sulphate of ammonia can be obtained at a cheap rate (as in the neighbourhood of the gas-works), it is very commonly substituted for the chloride of potassium, when *ammonia-alum* is obtained instead of *potash-alum*. The former is similar in all respects to the latter salt, except that it contains the hypothetical metal ammonium (NH_4) in place of potassium, and its formula is, therefore, $Al_2O_3.3SO_3$, $(NH_4)_2O.SO_3.24Aq$.

For all the uses of alum, in dyeing and calico-printing, in paper-making and in the manufacture of colours, ammonia-alum answers quite as well as potash-alum, and hence both these salts are sold under the common name of alum.

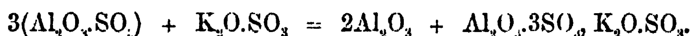
These alums are the representatives of an important class of double sulphates, composed of a sulphate of one of the alkalies combined with the normal sulphate of a sesquioxide. They all contain 24 molecules of water of crystallisation, and their crystalline form is that of the cube or octahedron.

When a solution of alum is mixed with a little solution of carbonate of soda, a precipitate of alumina is formed, which redissolves when the solution is stirred. If the addition of carbonate of soda be continued as long as the precipitate redissolves when stirred, the salt $Al_2O_3.SO_3$ will remain in the solution—



$$Al_2O_3.3SO_3, K_2O.SO_3 + 2(Na_2O.CO_2) = Al_2O_3.SO_3 + 2(Na_2O.SO_3) + K_2O.SO_3 + 2CO_2.$$

This solution of *basic alum*, as it is called, is decomposed by boiling, alumina being deposited and ordinary alum remaining in solution—



$$3(Al_2O_3.SO_3) + K_2O.SO_3 = 2Al_2O_3 + Al_2O_3.3SO_3, K_2O.SO_3.$$

When stuffs are immersed in the solution of basic alum they also withdraw a portion of alumina, which becomes fixed in their fibre, and serves as a mordant to attract and fix the colouring matter when the stuff is transferred to a dye-bath.

Alumina.—When ammonia-alum is strongly heated, it loses the whole of its water, ammonia,* and sulphuric acid, leaving merely a white insoluble earthy substance which is alumina itself (Al_2O_3), and differs widely from the metallic oxides which have been hitherto considered, by the feebly basic character which it exhibits. Not only is alumina destitute of alkaline properties, but it is not even capable of entirely neutralising the acids, and hence both sulphate of alumina and alum are exceedingly acid salts.

Pure crystallised alumina is found in nature as the mineral *corundum*, distinguished by its extreme hardness, in which it ranks next to the diamond. An opaque and impure variety of corundum constitutes the very useful substance *emery*. The *ruby* and *sapphire*† consist of nearly pure alumina; *spinelle* is a compound of magnesia with alumina, $MgO.Al_2O_3$; whilst in the *topaz* the alumina is associated with silica and fluoride of aluminum. The mineral *diaspore* is a hydrate of alumina

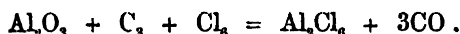
* The great absorption and disappearance of heat during the evaporation of the water and ammonia from this alum, has led to its employment for filling the space between the double walls of fire-proof safes, which may become red-hot outside, whilst the inside is kept below the scorching-point of paper.

† Small crystals of alumina resembling natural sapphire have been obtained by the action of vapour of fluoride of aluminum upon boracic acid at a high temperature. By adding a little fluoride of chromium, crystals similar to rubies and emeralds have been produced.

($Al_2O_3.2H_2O$), so named from its falling to powder when heated (*διασπορα, dispersion*).

The artificially prepared hydrate of alumina is characterised by its gelatinous appearance. If a little alum be dissolved in warm water, and some ammonia added to the solution, the ammonia will combine with the sulphuric acid, whilst the alumina will unite with water to form a semi-transparent gelatinous mass of hydrate of alumina ($Al_2O_3.3H_2O$). When washed and dried, it shrinks very much and forms a mass resembling gum. The hydrate of alumina has a great attraction for most colouring matters, with which it forms insoluble compounds called *lakes*. Thus, if a solution of alum be mixed with infusion of *logwood*, and a little ammonia added, the hydrate of alumina will form, with the colouring matter, a purplish-red *lake*, which may be filtered off, leaving the solution colourless. This property is turned to advantage in calico-printing, where the compounds of alumina are largely used as mordants.

Chloride of aluminum.—If the alumina obtained by calcining ammonia-alum be intimately mixed with charcoal, and strongly heated in an earthen tube or retort through which a stream of well-dried chlorine is passed, the oxygen of the alumina is abstracted by the charcoal, to form carbonic oxide, whilst the chlorine combines with the aluminum yielding chloride of aluminum (Al_2Cl_6) which passes off in vapour and may be condensed, in an appropriate receiver, as a white crystalline solid—



$$Al_2O_3 + C_3 + Cl_6 = Al_2Cl_6 + 3CO.$$

This formation of the chloride of aluminum is possessed of some interest, as an example of the decomposition of a compound body by the co-operation of two elements, neither of which alone would be able to decompose the compound; neither carbon nor chlorine would, alone, decompose alumina, however high the temperature, but when the attraction of the carbon for the oxygen is added to that of the chlorine for the aluminum, the decomposition is easily effected.

An impure solution of chloride of aluminum is sold as a disinfectant under the name of *chloralum*.

But this chloride of aluminum also deserves attention as being the source from which the metal aluminum may be prepared in large quantities.

201. *Aluminum.*—In order to obtain this interesting metal, it is only necessary to pass the chloride of aluminum in the state of vapour over heated sodium, which removes the chlorine in the form of chloride of sodium, leaving the aluminum as a white malleable metal about as hard as zinc, and fusing at a somewhat lower temperature than silver. For the extraction of aluminum upon the large scale, the alumina is not prepared from alum, but from the mineral known as *Bauxite*, which contains alumina, together with peroxide of iron and silica.* This mineral is heated with soda-ash (see p. 264), when carbonic acid escapes, and the silica and alumina combine with soda to form silicate of soda, and a soluble compound of alumina with soda, which is generally called *aluminate of soda*, and has the composition $3Na_2O.Al_2O_3$. On treating the mass with water, an insoluble silicate of alumina and soda is left, whilst the aluminate of soda is dissolved, and is obtained as an infusible mass when the solution is evaporated. This aluminate of soda is largely used by calico-printers as a mordant. To obtain alumina from it, the solution is neutralised with hydrochloric acid, which converts the sodium into chloride, and precipitates the alumina as hydrate of alumina ($Al_2O_3.3H_2O$).

* This mineral is found at Baux, near Arles, in the south of France, and contains silica 13 to 17 per cent., alumina 60 to 65, peroxide of iron 4 to 8, water 15 to 17.

As the next step towards the preparation of aluminum, the hydrate of alumina is mixed with charcoal and common salt, made up into balls, dried, and strongly heated in earthen cylinders through which dry chlorine is passed. The carbon abstracts the oxygen from the alumina, forming carbonic oxide, whilst the aluminum combines with the chlorine, and the chloride of aluminum so formed combines with the chloride of sodium, and distils over as the *double chloride of aluminum and sodium* ($Al_2Cl_6.2NaCl$). This salt is then mixed with a proper proportion of metallic sodium, and heated in a reverberatory furnace, when the sodium combines with the chlorine of the chloride of aluminum, leaving the latter metal to separate in a fused state beneath the melted chloride of sodium, which protects it from oxidation. The aluminum may be rolled into sheets or drawn into wire. Commercial aluminum has been found to contain from 3 to 7·5 per cent. of iron. Silicon is also present in it, as much as 14 per cent. having been found in one sample.

Aluminum is much more sonorous than most other metals. A bar of it suspended from a string, and struck with a hammer, emits a clear musical sound. It is remarkable as being the lightest metal capable of resisting the action of air even in the presence of moisture. Its specific gravity is 2·5. This lightness renders it valuable for the manufacture of small weights, such as the grain and its fractions, since these, when made of aluminum, are more than three times as large as when made of brass, and nearly nine times as large as platinum weights of the same denomination. It is also employed for ornamental purposes, for though not so brilliant as silver, it is not blackened by sulphuretted hydrogen, which so easily affects that metal (p. 196).

Another characteristic feature of aluminum is its comparative resistance to the action of nitric acid even at a boiling heat. No other metal commonly met with, except platinum and gold, is capable of resisting the action of nitric acid to the same extent. Hydrochloric acid, however, which will not attack gold and platinum, dissolves aluminum with facility, converting it into chloride of aluminum, with disengagement of hydrogen; $Al_2 + 6HCl = Al_2Cl_6 + H_6$. Solutions of potash and soda also easily dissolve it, forming the so-called aluminates of those alkalies; thus $3(Na_2O.H_2O) + Al_2 = 3Na_2O.Al_2O_3 + H_6$. Even when very strongly heated in air, aluminum is oxidised to a very slight extent, probably because the coating of alumina which is formed remains infusible and protects the metal beneath it. For a similar reason, apparently, aluminum decomposes steam slowly, even at a high temperature.

When aluminum is fused with nine times its weight of copper, it forms an alloy very similar to gold in appearance, but almost as strong as iron. This alloy was strongly recommended to replace gold for ornamental purposes, but it does not retain its brilliancy so completely as that metal. Aluminum does not unite with mercury or with melted lead, both of which are capable of dissolving nearly all other metals.

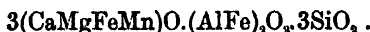
202. *Mineral silicates of alumina.*—Many of the chemical formulæ of minerals, which contain silicates of alumina associated with the silicates of other metallic oxides, are complicated, from the circumstance that a part of the aluminum is often replaced by iron, which, in the form of sesquioxide (Fe_2O_3), is isomorphous with it, and therefore capable of replacing it without altering the crystalline form and general character of the mineral. In a similar manner, the other metals present in the mineral

may be exchanged for isomorphous representatives; thus there are two well-known feldspars, potash-feldspar (*orthoclase*) and soda-feldspar (*albite*), having the formulæ $K_2O.Al_2O_3.6SiO_2$, and $Na_2O.Al_2O_3.6SiO_2$. These minerals are sometimes mingled in one and the same crystal (*potash-albite* or *pericline*) without bearing any definite equivalent proportion to each other; the formula of such a mineral would be written $(KNa)_2O.Al_2O_3 6SiO_2$.

Porphyry has the same chemical composition as feldspar.

Mica, again, is composed essentially of magnesia, alumina, and silica ($4MgO.Al_2O_3.4SiO_2$), but part of the magnesium is so constantly replaced by potassium and iron (as protoxide), and part of the aluminum by iron (as sesquioxide), that the general formula for mica must be written $4(K_2MgFe)O.(AlFe)_2O_3.4SiO_2$.

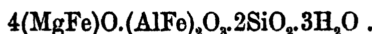
Garnet is essentially a double silicate of alumina and lime, but often contains magnesium, iron, or manganese, replacing part of the calcium, and iron replacing part of the aluminum, being written—



$$3(CaMgFeMn)O.(AlFe)_2O_3.3SiO_2\ .$$

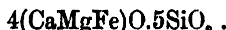
This mineral is sometimes formed artificially in the slag of the iron blast-furnaces.

Chlorite, a very important variety of rock, is a double silicate of alumina and magnesia, with variations as expressed by the formula—



$$4(MgFe)O.(AlFe)_2O_3.2SiO_2.3H_2O\ .$$

Basalt is a feldspathic rock containing crystals of *augite*—



$$4(CaMgFe)O.5SiO_2\ .$$

Gneiss is chemically composed like granite, but the mica is arranged in regular layers. *Trap* rock contains feldspar, together with *hornblende* which consists of silicates of alumina, lime, magnesia, and oxide of iron. Hornblende is sometimes found replacing the mica in granite, forming the rock called *syenite*.

Lapis lazuli, the valuable mineral which furnishes the natural ultramarine used in painting, consists chiefly of silica and alumina, which constitute respectively 45 and 32 per cent. of it, but there are also present 9 per cent. of soda, 6 per cent. of sulphuric acid, about 1 per cent. of sulphur, and a somewhat smaller quantity of iron, together with a variable proportion of lime. The cause of its blue colour is not understood, since neither of its predominant constituents is concerned in the production of such a colour in other cases. In consequence of the rarity of the mineral, the natural ultramarine bears a very high price, but the *artificial ultramarine* is manufactured in very large quantities at a low cost, and forms a very good imitation. One of the processes for preparing it consists in heating to bright redness in a covered crucible, for three or four hours, an intimate mixture of 100 parts of pure white clay (kaolin), 100 of dried carbonate of soda, 60 of sulphur, and 12 of charcoal. This would be expected to yield a mixture of silicate of soda, aluminate of soda, and sulphide of sodium, the two first being white, and the latter yellow or brown, but the mass is found to have a *green* colour (*green ultramarine*). It is finely powdered, washed with water, dried, mixed with a fifth of its weight of sulphur, and gently roasted in a thin layer till the sulphur has burnt off, this operation being repeated, with fresh additions of sulphur, until the

residue has a fine blue colour. In the opinion of some chemists, the presence of a small proportion of iron is essential to the blue colour, while others believe the colour to be due to sulphide of sodium or hyposulphite of soda, or both. Ultramarine is a very permanent colour under ordinary conditions of exposure to air and light, but acids bleach it at once, with separation of gelatinous silica and evolution of sulphuretted hydrogen. Blue writing paper is often coloured with ultramarine, so that its colour is discharged by acids falling upon it in the laboratory. Chlorine also bleaches ultramarine. Starch is often coloured blue with this substance.

Phosphate of alumina is found naturally in several forms. It occurs in large quantities in the West India Islands. *Turquoise* is a hydrated phosphate of alumina ($Al_2O_3.P_2O_5$), owing its colour to the presence of oxide of copper.* *Wavellite* has the composition $3Al_2O_3.2P_2O_5$. None of the earlier analysts detected the phosphoric acid in this mineral, on account of the difficulty in separating it from the alumina, so that even in comparatively modern chemical works, it is described as a hydrate of alumina.

GLUCINUM.

$Gl'' = 9{\cdot}5$ parts by weight.

203. This comparatively rare metal (which derives its name from the sweet taste of its salts, γλυκύς, *sweet*) is found associated with silica and alumina in the *emerald*, which is a double silicate of alumina and glucina, $Al_2O_3.3SiO_2$, $3(GlO.SiO_2)$, and appears to owe its colour to the presence of a minute quantity of oxide of chromium. The more common mineral *beryl* has a similar composition, but is of a paler green colour, apparently caused by protoxide of iron. *Chrysoberyl* consists of glucina and alumina, also coloured by iron. The earlier analysts of these minerals mistook the glucina for alumina, which it resembles in forming a gelatinous precipitate on adding ammonia to its solutions, but it is a stronger base than alumina, and is therefore capable of displacing ammonia from its salts, and of being dissolved by them. Carbonate of ammonia is employed to separate the glucina from alumina, since it dissolves the glucina in the cold, forming a double carbonate of glucina and ammonia, from which the carbonate of glucina is precipitated on boiling. Glucina (GlO) is intermediate in properties between alumina and magnesia, resembling the latter in its tendency to absorb carbonic acid from the air, and to form soluble double salts with the salts of ammonia, and so much resembling alumina in the gelatinous form of its hydrate, its solubility in alkalies, and the sweet astringent taste of its salts, that it was formerly regarded as a sesquioxide like alumina.

The metal itself is very similar to aluminum.

204. THORINUM is present in a rare Norwegian mineral, *thorite*, where it is associated with silica, lime, magnesia, and other metallic oxides. The metal itself is similar to aluminum, but its oxide *thorina* appears to be a protoxide (ThO), and differs from alumina and glucina in being *insoluble in the alkalies* (potash, for example), though it dissolves in carbonate of potash. Moreover, the *sulphate of thorina* is sparingly soluble in hot water, so that it is precipitated on boiling its solution.

205. YTTRIUM and ERBIUM are very rare metals found in *gadolinite*, a mineral silicate occurring at Ytterby in Sweden, and containing beside these, glucinum, cerium, and iron. Their oxides *yttria* (YO) and *erbia* resemble thorina in being insoluble in the alkalies, but soluble in their carbonates; yttria is white, but erbia has a yellow colour. The salts of yttria and erbia are colourless.

206. CERIUM is also found in gadolinite, but more abundantly in *cerite*, which is essentially a silicate of cerium. Phosphate of cerium (*cryptolite*) has also been found in brown apatite. This metal has been employed medicinally, in the form of oxalate

* False or bone turquoise is fossil ivory, owing its colour to the presence of the natural blue phosphate of iron.

of cerium ($CeO.C_2O_3.3H_2O$. It forms two basic oxides, CeO, which is white, and forms colourless salts, and Ce_2O_3, which is yellow, and gives yellow or red salts. In this respect, cerium more nearly resembles iron than aluminum. These oxides of cerium are insoluble in the alkalies; the protoxide is easily precipitated from its salts by oxalic acid in the form of the oxalate mentioned above. Sesquioxide of cerium does not appear to form a corresponding chloride, but yields protochloride of cerium and free chlorine when heated with hydrochloric acid.

LANTHANIUM (from λανθάνω, *to escape notice*) is also found in cerite, but it differs from cerium in forming only one oxide, which is white in the hydrated, but buff in the anhydrous state. When a mixture of nitrates of cerium and lanthanium is calcined, sesquioxide of cerium and oxide of lanthanium are left, and may be separated by treatment with nitric acid, diluted with 100 parts of water, which dissolves only the latter.

DIDYMIUM (δίδυμος, *twin*) is very similar to lanthanium, which is associated with it in cerite. It also forms but one oxide, which is violet when hydrated, and brown when anhydrous. It is insoluble in potash. The salts of didymium are either pink or violet.

207. ZIRCONIUM exists in the rare minerals *zircon* and *hyacinth*, in which its oxide *zirconia* (ZrO_2) is combined with silicic acid. Zirconia is somewhat similar to alumina, but is insoluble in potash, and dissolves in carbonate of potash. Its sulphate, moreover, is decomposed by boiling with sulphate of potash, which removes part of the sulphuric acid, forming bisulphate of potash, and precipitates basic sulphate of zirconia. Metallic zirconium somewhat resembles amorphous silicon, but it decomposes water slowly at the boiling point, and has not been fused.

ZINC.

Zn'' = 65 parts by weight.

208. Zinc occupies a high position among useful metals, being peculiarly fitted, on account of its lightness, for the construction of gutters, water-pipes, and roofs of buildings, and possessing for these purposes a great advantage over lead, since the specific gravity of the latter metal is about 11·5, whilst that of zinc is only 6·9. For such applications as these, where great strength is not required, zinc is preferable to iron, on account of its superior malleability; for although a bar of zinc breaks under the hammer at the ordinary temperature, it becomes so malleable at 250° F as to admit of being rolled into thin sheets. This malleability of zinc when heated was discovered only in the commencement of this century, until which time the only use of the metal was in the manufacture of brass. When zinc is heated to 400° F., it again becomes brittle. The easy fusibility of zinc also gives it a great advantage over iron, as rendering it easy to be cast into any desired form; indeed, zinc is surpassed in fusibility (among the metals in ordinary use) only by tin and lead, its melting point being below a red heat, and usually estimated at 770° F. Zinc is also less liable than iron to corrosion under the influence of moist air, for although a bright surface of zinc soon tarnishes when exposed to the air, it merely becomes covered with a thin film of oxide of zinc (passing gradually into basic carbonate, by absorption of carbonic acid from the air) which protects the metal from further action.

The great strength of iron has been ingeniously combined with the durability of zinc, in the so-called *galvanised iron*, which is made by coating clean iron with melted zinc, thus affording a protection much needed in and around large towns, where the sulphurous and sulphuric acids arising from the combustion of coal, and the acid emanations from various factories, greatly accelerate the corrosion of unprotected iron. The iron plates to be coated are first thoroughly cleansed by a process which will be more particularly noticed in the manufacture of tin-plate, and are then

dipped into a vessel of melted zinc, the surface of which is coated with sal-ammoniac (hydrochlorate of ammonia) in order to dissolve the oxide of zinc which forms upon the surface of the melted metal, and might adhere to the iron plate so as to prevent its becoming uniformly coated with the zinc.* A more firmly adherent coating of zinc is obtained by first depositing a thin film of tin upon the surface of the iron plate by galvanic action, and hence the name of *galvanised* iron.

The ores of zinc are found pretty abundantly in England, chiefly in the Mendip Hills in Somersetshire, at Alston Moor in Cumberland, in Cornwall and Derbyshire, but the greater part of the zinc used in this country is imported from Belgium and Germany, being derived from the ores of Transylvania, Hungary, and Silesia.

Metallic zinc is never met with in nature. Its chief ores are *calamine* or carbonate of zinc ($ZnO.CO_2$), *blende* or sulphide of zinc (ZnS), and *red zinc ore*, in which oxide of zinc (ZnO) is associated with the oxides of iron and manganese.

Calamine is so called from its tendency to form masses resembling a bundle of reeds (*calamus, a reed*). It is found in considerable quantities in Somersetshire, Cumberland, and Derbyshire. A compound of carbonate with hydrate of zinc, $ZnO.CO_2, 2(ZnO.H_2O)$ is found abundantly in Spain. The mineral known as *electric calamine* is a silicate of zinc ($2ZnO.SiO_2.H_2O$). Blende derives its name from the German *blenden, to dazzle*, in allusion to the brilliancy of its crystals, which are generally almost black from the presence of sulphide of iron, the true colour of pure sulphide of zinc being white. Blende is found in Cornwall, Cumberland, Derbyshire, Wales, and the Isle of Man, and is generally associated with galena or sulphide of lead, which is always carefully picked out of the ore before smelting it, since it would become converted into oxide of lead, which corrodes the earthen crucibles employed in the process.

In England, the extraction of zinc from its ores is carried on chiefly at Swansea, Birmingham, and Sheffield. Before extracting the metal from these ores, they are subjected to a preliminary treatment, which brings them both to the condition of oxide of zinc. For this purpose the calamine is simply calcined in a reverberatory furnace, in order to expel the carbonic acid; but the blende is *roasted* for ten or twelve hours, with constant stirring, so as to expose fresh surfaces to the air, when the sulphur passes off in the form of sulphurous acid, and its place is taken by the oxygen, the ZnS becoming ZnO. The extraction of the metal from this oxide of zinc depends upon the circumstance that zinc is capable of being distilled at a bright red heat, its boiling point being 1904° F.

The facility with which this metal passes off in the form of vapour is seen when it is melted in a ladle over a brisk fire, for at a bright red heat abundance of vapour rises from it, which, taking fire in the air, burns with a brilliant greenish white light, throwing off into the air numerous white flakes of light oxide of zinc (the philosopher's wool, or *nil album* of the old chemists).

The distillation of zinc may be effected on the small scale in a black-lead crucible (A, fig. 241) about 5 inches high and 3 in diameter. A hole is drilled through the bottom with a round file, and into this is fitted a piece of wrought-iron gas-pipe (B) about 9 inches long and 1 inch wide, so as to reach nearly to the top of the inside of

* The sal-ammoniac acts upon the heated zinc according to the equation, $Zn + 2(NH_3.HCl) = ZnCl_2 + 2NH_3 + H_2$, and the chloride of zinc which is formed dissolves the oxide from the surface of the metal, producing an oxychloride of zinc.

the crucible. Any crevices between the pipe and the sides of the hole are carefully stopped up with fire-clay moistened with solution of borax. A few ounces of zinc are introduced into the crucible, the cover of which is then carefully cemented on with fire-clay (a little borax being added to bind it together at a high temperature), and the hole in the cover is stopped up with fire-clay. The crucible having been kept for several hours in a warm place, so that the clay may dry, it is placed in a cylindrical furnace with a hole at the bottom, through which the iron pipe may pass, and a lateral opening into which is inserted an iron tube (C) connected with a forge bellows. Some lighted charcoal is thrown into the furnace, and when this has been blown into a blaze, the furnace is filled up with coke broken into small pieces. The fire is then blown till the zinc distils freely into a vessel of water placed for its reception. Four ounces of zinc may be easily distilled in half-an-hour.

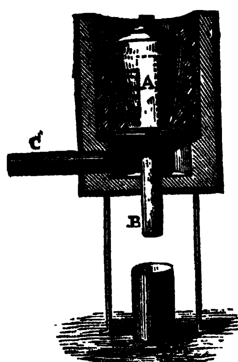


Fig. 241.—Distillation of zinc.

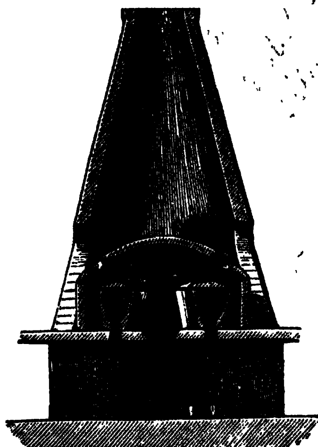


Fig. 242.—English zinc furnace.

English method of extracting zinc.—The oxide of zinc, obtained as above from calamine or blende, is mixed with about half its weight of coke or anthracite coal. This mixture is introduced into large crucibles (fig. 242) with a hole in the bottom, through which passes a short wide iron pipe destined for the passage of the vapour of zinc. These crucibles are about 4 feet high by 2½ feet wide. Some large pieces of coke are first introduced into them to prevent the charge from passing into the iron pipes, and when they have been charged with the above mixture, their covers are cemented on, and they are heated in furnaces somewhat resembling those of a glass-house, each furnace receiving six crucibles, which generally contain, in all, one ton of roasted ore. When the mixture in the crucibles is heated to redness, it begins to evolve carbonic oxide, produced by the combination of the carbon with the oxygen from the oxide of zinc. This gas burns with a blue flame at the mouth of the iron pipe; but at a bright red heat the metallic zinc which has been thus liberated is converted into vapour, and the greenish-white flame of burning zinc is perceived at the orifice. When this is the case, about 8 feet of iron pipe are joined on to the short piece, in order to condense the vapour of zinc, which falls into a vessel placed for its reception. The distillation occupies about sixty hours, and the average yield is about 35 parts of zinc from 100 of ore, a considerable quantity of zinc being left behind in the form of silicate of zinc (electric calamine), which is not reduced by distillation with carbon.

The zinc thus obtained, however, is mixed with a considerable quantity of oxide of zinc, and with other foreign matters carried over from the crucibles. It is, therefore, again melted in a large iron pan, and allowed to rest, in order that the dross may rise to the surface; this is skimmed off, to be worked over again in a fresh operation, and the metal is cast into ingots, which are sent into commerce under the name of *spelter*.

Belgian process for the extraction of zinc.—At the Vieille-Montagne works, near Liége, calamine is exposed to the rain for several months in order to wash out the clay; it is then calcined to expel the water and carbonic acid, the oxide of zinc so obtained being mixed with half its weight of coal dust, and distilled in fire-clay cylinders (C, fig. 243), holding about 40 lbs. each, and set in seven tiers of six each in the same furnace, the vapour of zinc being conveyed by a short conical iron pipe (B) into a conical iron receiver (D), which is emptied every two hours into a large ladle, from which the zinc is poured into ingot-moulds. Each distillation occupies about twelve hours. The advantage of this particular mode of arranging the cylinders is, that it economises fuel by allowing the poorer ores, which require less heat to distil all the zinc from them, to be introduced into the upper rows of cylinders farthest from the fire (A). There are two varieties of Belgian ore, one containing 33 and the other 46 per cent. of zinc, but a large proportion of this is in the form of silicate, which is not extracted by the distillation.

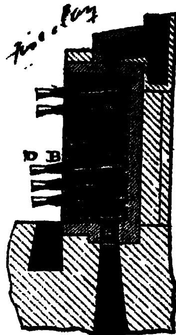
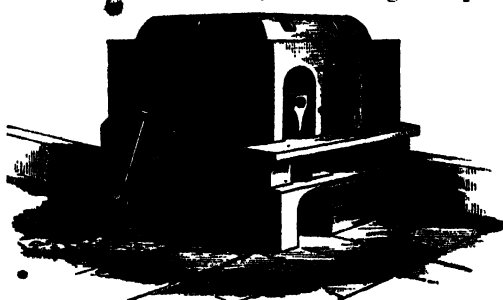


Fig. 243.—Belgian zinc furnace.

Silesian process for extracting zinc.—In Silesia, the oxide of zinc obtained by the calcination of calamine is mixed with fine cinders, and distilled in arched earthen retorts (A, fig. 244), into which the charge is introduced through a small door (B), which is then cemented up. These retorts are arranged in a double row in the same furnace (fig. 245), and the vapour of zinc is condensed in a bent earthenware pipe attached to each retort, and having an opening (C) near the bend, which is kept closed, unless it is necessary to clear out the pipe. In regard to the consumption of fuel, this process is far more economical than that followed in this country. The Silesian zinc is remelted, before casting into ingots, in clay instead of iron pots, since melted zinc always dissolves iron, and a very small quantity of that metal is found to injure zinc when required for rolling into sheets.



Fig. 244.


Fig. 245.—Silesian zinc furnace.

A small quantity of lead always distils over together with the zinc,

and since this metal also interferes with the rolling of zinc into sheets, a portion of it is separated from zinc intended for this purpose, by melting the spelter, in large quantity, upon the hearth of a reverberatory furnace, the bed of which is inclined so as to form a deep cavity at the end nearest the chimney. The specific gravity of lead being 11·4, whilst that of zinc is 6·9, the former accumulates chiefly at the bottom of the cavity, and the ingots cast from the upper part of the melted zinc will contain but little lead, since zinc is not able to dissolve more than 1·2 per cent. of that metal.

Ingots of zinc, when broken across, exhibit a beautiful crystalline fracture, which, taken in conjunction with the bluish colour of the metal, enables it to be easily identified.

The spelter of commerce is liable to contain lead, iron, tin, antimony, arsenic, copper, and cadmium. Belgian zinc is usually purer than the English metal.

Zinc being easily dissolved by diluted acids, it is necessary to be careful in employing this metal for culinary purposes, since its soluble salts are poisonous.

It will be remembered that the action of diluted sulphuric acid upon zinc is employed for the preparation of hydrogen. Pure zinc, however, evolves hydrogen very slowly, since it becomes covered with a number of hydrogen bubbles which protect it from further action; but if a piece of copper or platinum be made to touch the zinc beneath the acid, these metals, being electronegative towards the zinc, will attract the electropositive hydrogen, leaving the zinc free from bubbles and exposed on all points to the action of the acid, so that a continuous disengagement of hydrogen is maintained. As a curious illustration of this, a thin sheet of platinum or silver foil may be shown to sink in diluted sulphuric acid, until it comes in contact with a piece of zinc, when the bubbles of hydrogen bring it up to the surface. The lead, iron, &c., met with in commercial zinc, are electronegative to the zinc, and thus serve to maintain a constant evolution of hydrogen.

A coating of metallic zinc may be deposited upon copper by slow galvanic action, if the copper be immersed in a concentrated solution of potash, at the boiling point of water, in contact with metallic zinc, when a portion of the latter is dissolved in the form of oxide, with evolution of hydrogen, and is afterwards precipitated on the surface of the electronegative copper.

Oxide of zinc (ZnO).—Zinc forms but one oxide, which is known in commerce as *zinc-white*, and is prepared by allowing the vapour of the metal to burn in earthen chambers through which a current of air is maintained. This zinc-white is sometimes used for painting in place of white lead (carbonate of lead), over which it has the advantages of not injuring the health of the persons using it, and of being unaffected by sulphuretted hydrogen, an important consideration in manufacturing towns where that substance is so abundantly supplied to the atmosphere. Unfortunately, however, the oxide of zinc does not combine with the oil of the paint, as oxide of lead does, and the paint is consequently more liable to peel off. The oxide of zinc has the characteristic property of becoming yellow when heated, and white again as it cools. It is sometimes used in the manufacture of glass for optical purposes.

Oxide of zinc forms a soluble compound with potash, in this respect resembling alumina, and therefore metallic zinc, like aluminum, is dis-

solved by boiling with solution of potash, hydrogen being disengaged from the water, the oxygen of which combines with the zinc.

The *sulphate of zinc* or *white vitriol*, which is employed in medicine, and more extensively in calico-printing, is prepared by roasting blende (sulphide of zinc, ZnS) at a low temperature, when both its elements combine with oxygen, the oxide of zinc and sulphuric acid thus produced remaining in combination as sulphate of oxide of zinc ($ZnO.SO_3$). After roasting, the mass is treated with water, which dissolves the sulphate, and yields it again, on evaporation, in prismatic crystals having the formula $ZnO.SO_3.H_2O.6Aq$.

Chloride of zinc ($ZnCl_2$), prepared by dissolving zinc in hydrochloric acid, is known in commerce as *Burnett's disinfecting fluid*, since it is capable of absorbing hydrosulphuric acid, ammonia, and other offensive products of putrefaction, and arrests the decomposition of wood and animal substances. By evaporating its solution, the chloride of zinc is obtained in a fused state, and solidifies on cooling into white deliquescent masses. It has a very powerful attraction for water.

CADMIUM.

Cd″ = 112 parts by weight.*

209. This metal is found in small quantities in the ores of zinc, its presence being indicated during the extraction of that metal (p. 294) by the appearance of a brown flame (*brown blaze*) at the commencement of the distillation, before the characteristic zinc-flame is seen at the orifice of the iron tube. Cadmium is more easily vaporised than zinc, boiling at 1580° F., so that the bulk of it is found in the first portions of the distilled metal. If the mixture of cadmium and zinc be dissolved in diluted sulphuric acid, and the solution treated with hydrosulphuric acid gas, a bright yellow precipitate of *sulphide of cadmium* (CdS) is obtained, which is employed in painting under the name of *cadmia*. By dissolving this in strong hydrochloric acid and adding carbonate of ammonia, the carbonate of cadmium ($CdO.CO_2$) is precipitated, from which metallic cadmium may be extracted by distillation with charcoal.

Although resembling zinc in its volatility and its chemical relations, in appearance it is much more similar to tin, and emits a crackling sound like that metal when bent. Like tin, also, it is malleable and ductile at the ordinary temperature, and becomes brittle at about 180° F. It is as fusible as tin, becoming liquid at 442° F., so that it is useful for making fusible alloys. An alloy of 3 parts of cadmium with 15 of bismuth, 8 of lead, and 4 of tin, fuses at 140° F. In its behaviour with acids and alkalies cadmium is similar to zinc, but the metal is easily distinguished from all others by its yielding a characteristic chestnut-brown oxide when heated in air. This oxide (CdO) is the only oxide of cadmium.

The *iodide of cadmium* (CdI_2), obtained by the action of iodine upon the metal in the presence of water, is employed in photography.

INDIUM is the name of a metal which has recently been discovered, with the help of the spectroscope, in a specimen of blende from Freiberg. Its name refers to an indigo blue line in the spectrum. The examination of the metal is as yet imperfect, but it is white, malleable, and dissolves, like zinc and cadmium, in hydrochloric acid. Its specific gravity is 7·36. To extract indium from the Freiberg zinc, the metal is

* 112 parts by weight of cadmium, when converted into vapour, occupy *twice* the volume of one part by weight of hydrogen, making it appear that its atomic weight should be 56, but the specific heat of cadmium, as well as its general chemical relations, favour the view that it is a di-atomic metal like zinc, its atomic weight being 112.

boiled with dilute sulphuric acid, employed in such quantity as to leave part of the zinc undissolved, together with indium and lead. The residue is dissolved in nitric acid, the lead and cadmium precipitated by hydrosulphuric acid, the latter expelled by boiling, and the oxide of indium precipitated from the solution by carbonate of baryta. When this precipitate is dissolved in hydrochloric acid, and excess of ammonia added, the white hydrated oxide of indium is precipitated, and may be reduced by heating in hydrogen.

At a bright red heat it burns with a violet blue flame, yielding a yellow oxide of indium, InO.

The atomic weight of indium appears to be about 72.

210. URANIUM.—This is a rare metal, never employed in the metallic state, but in the form of sesquioxide (U_2O_3) and black oxide ($2UO.U_2O_3$), for imparting yellow and black colours respectively to glass and porcelain. The chief source of these compounds is the mineral *pitch-blende,* which contains a large proportion of black oxide of uranium, together with silica, iron, copper, lead, and arsenic. In its chemical relations uranium presents some similarity to iron and manganese. It forms two distinct oxides, UO and U_2O_3, of which the former is decidedly basic, whilst the latter is capable of acting both as an acid and a base. The bright greenish-yellow colour of the salts of the sesquioxide of uranium is characteristic of the metal, and glass coloured with this oxide exhibits the remarkable optical effect of fluorescence in a very high degree.

IRON.

$Fe'' = 56$ parts by weight.

211. This most useful of all metals is one of those most widely and abundantly diffused in nature. It is to be found in nearly all forms of rock, clay, sand, and earth, its presence in these being commonly indicated by their colours, for iron is the commonest of natural mineral colouring ingredients. It is also found, though in small proportion, in plants, and in larger quantity in the bodies of animals, especially in the blood, which contains about 0·5 per cent. of iron in very intimate association with its colouring matter.

But iron is very rarely found in the metallic state in nature, being almost invariably combined either with oxygen or sulphur.

Metallic iron is met with, however, in the *meteorites* or metallic masses, sometimes of enormous size, and of unknown origin, which occasionally fall upon the earth. Of these iron is the chief component, but there are also generally present, cobalt, nickel, chromium, manganese, copper, tin, magnesium, carbon, phosphorus, and sulphur.

The chief forms of combination in which iron is found in sufficient abundance to render them available as sources of the metal, are shown in the following table:—

Ores of Iron.

Common Name.	Chemical Name.	Composition.
Magnetic iron ore	Protosesquioxide of iron	Fe_3O_4
Red hæmatite	Sesquioxide of iron	Fe_2O_3
Specular iron	" "	"
Brown hæmatite	Hydrated sesquioxide	$2Fe_2O_3.3H_2O$
Spathic iron ore	Carbonate of iron	$FeO.CO_2$.
Clay iron-stone	Carbonate of iron with clay	
Blackband	Carbonate of iron with clay and bituminous matter	
Iron pyrites	Bisulphide of iron	FeS_2

These ores are frequently associated with extraneous minerals, some of the constituents of which are productive of injury to the quality of the iron. It is worthy of notice that scarcely one of the ores of iron is entirely free from sulphur and phosphorus, substances which will be seen to have a very serious influence on the quality of the iron extracted from them, and the presence of which increases the difficulty of obtaining the metal in a marketable condition.

The following table illustrates the general composition of the most important English ores of iron, with reference to the proportions of iron, and of those substances which materially influence the character of the iron extracted from the ore, viz., manganese (present as oxide or carbonate), phosphorus (present as phosphoric acid), and sulphur (present as bisulphide of iron). The maximum and minimum quantites found in each ore are specified.

*British Iron Ores.**

In 100 parts.	Iron.		Oxide of Manganese.		Phosphoric Acid.		Bisulphide of Iron. (Pyrites.)		No. of Samples Analysed.
	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	
Clay iron-stone from coal measures,	43·30	20·95	3 30	0·46	1·42	0·07	1·21	0	77
Clay iron-stone from the lias,	49·17	17·34	1·30	0	5·05	0	1·60	0	12
Brown hæmatite, ...	63·04	11·98	1·60	trace	3·17	0	0·30	0	23
Red hæmatite, . .	69 10	47·47	1·18	trace	trace	trace	0·06	0	5
Spathic ore, . . .	49·78	13·98	12·64	1·93	0·22	0	0·11	0	6
Magnetic ore, ...	57·01		0·14		0·10		0.07		1

From this table it will be gathered that, among the most abundant of the iron ores of this country, red hæmatite is the richest and purest, whilst the brown hæmatite often contains considerable proportions of sulphur and phosphorus, and the spathic ore, though containing little sulphur and phosphorus, often contains much manganese.

The argillaceous ores, or clay iron-stones, found in the lias, contain more phosphoric acid than those from the coal-measures; and these latter, as a general rule, contain more sulphur (pyrites) than the former, although the maximum in the table does not show this.

Clay iron-stone is the ore from which the largest quantity of iron is extracted in England, since it is found abundantly in the coal-measures of Staffordshire, Shropshire, and South Wales, and it is a circumstance of great importance in the economy of English iron-smelting, that the coal and lime-stone required in the smelting process, and even the fire-clay employed in the construction of the furnace, are found in the immediate vicinity of the ore.

Blackband is the clay iron-stone found in the coal-fields of Scotland, and often contains between 20 and 30 per cent. of bituminous matter, which contributes to the economy of fuel in smelting it.

Red hæmatite (Fe_2O_3) is the most characteristic of the ores of iron, occurring in hard shining rounded masses, with a peculiar fibrous structure and a dark red-brown colour, whence the ore derives its name (*αἷμα, blood*). It is found in considerable quantities in Lancashire and Cornwall, but

* This table has been compiled from the analyses given in "Percy on Iron and Steel."

unfortunately its very compact structure is an obstacle to its being smelted alone, so that it is generally mixed with some clay iron-stone, and hence the iron obtained is not so free from sulphur and phosphorus as if it were extracted from hæmatite alone.

Red ochre is a soft variety of this ore, containing a little clay.

Brown hæmatite ($2Fe_2O_3.3H_2O$) is found at Alston Moor (Cumberland) and in Durham, but it is more abundant on the Continent, and is the source of most of the Belgian and French irons. *Pea iron ore* and *yellow ochre* are varieties of brown hæmatite. The Scotch ore which is called *kidney-form clay iron-stone* is really a hydrated sesquioxide of iron.

Specular iron ore (Fe_2O_3) (*oligist ore* or *iron-glance*), although of the same composition as red hæmatite, is very different from it in appearance, having a steel-grey colour and a brilliant metallic lustre. The island of Elba is the chief locality where this ore is found, but it also occurs in Germany, France, and Russia. The excellent quality of the iron smelted from this ore is due partly to the purity of the ore, and partly to the circumstance that charcoal, and not coal, is employed in smelting it.

Magnetic iron ore (Fe_3O_4), of which the *loadstone* is a variety, has a more granular structure, and a dark iron-grey colour. It forms mountainous masses in Sweden, and is also found in Russia and North America. It is generally smelted with charcoal, and yields an excellent iron. *Iron sand*, a peculiar heavy black sand, of metallic lustre, consists in great measure of the magnetic ore, but contains a very large proportion of titanic acid. It is found abundantly in India, Nova Scotia, and New Zealand; but its fine state of division prevents it from being largely available as a source of iron.

Spathic iron ore ($FeO.CO_2$) is found in abundance in Saxony, and often contains a considerable quantity of carbonate of manganese, which influences the character of the metal extracted from it.

The *oolitic iron ore*, occurring in the Northampton oolite, contains both hydrated sesquioxide and carbonate of iron, together with clay.

Iron pyrites (FeS_2) is remarkable for its yellow colour, its brilliant metallic lustre, and crystalline structure, being generally found either in distinct cubical or dodecahedral crystals, or in rounded nodules of radiated structure. It was formerly disregarded as a source of iron, on account of the difficulty of separating the sulphur; but since the demand for iron has so largely increased, an inferior quality of the metal has been extracted from the residue left after burning the pyrites in the manufacture of oil of vitriol (p. 205), the residue being first well roasted in a lime-kiln to remove as much as possible of the sulphur.

212. *Metallurgy of iron.*—Iron owes the high position which it occupies among useful metals to a combination of valuable qualities not met with in any other. Although possessing nearly twice as great *tenacity* or *strength* as the strongest of the other metals commonly used in the metallic state, it is yet one of the lightest, its specific gravity being only 7·7, and is therefore particularly well adapted for the construction of bridges and large edifices, as well as for ships and carriages. It is the least yielding or malleable of the metals in common use, and can therefore be relied upon for affording a rigid support; and yet its ductility, when heated, is such that it admits of being rolled into the thinnest sheets and drawn into the finest wire, the strength of which is so great that a wire of $\frac{1}{10}$th inch in diameter is able to sustain 705 pounds, while a similar wire of

copper, which stands next in order of tenacity, will not support more than 385 pounds.

Being, with the exception of platinum, the least fusible of useful metals, iron is applicable to the construction of fire-grates and furnaces. Nor are its qualifications all dependent upon its physical properties, for it not only enters into a great number of compounds which are of the utmost use in the arts, but its chemical relations to one of the non-metallic elements, carbon, are such, that the addition of a small quantity of this element converts it into *steel*, far surpassing iron in the valuable properties of hardness and elasticity; whilst a larger quantity of carbon gives rise to *cast-iron*, the greater fusibility of which permits it to be moulded into vessels and shapes which could not be produced by forging.

213. *English process of smelting clay iron-stone.*—The first step towards the extraction of the metal consists in calcining (or *roasting*) the ore, in order to expel the water and carbonic acid which it contains. To effect this the ore is built up, together with a certain amount of small coal, into long pyramidal heaps, resting upon a foundation of large lumps of coal; blackband often contains so much coal that any further addition is unnecessary. These heaps are kindled in several places, and allowed to burn slowly until all the fuel is consumed. This calcination has the effect of rendering the ore more porous, and better fitted for the smelting process. If the ore contained much sulphur, a part of it would be expelled by the roasting, in the form of sulphurous acid.

Sometimes the calcination is effected in kilns resembling lime-kilns, and it is often altogether omitted as a separate process, the expulsion of the water and carbonic acid being then effected in the smelting-furnace itself as the ore descends.

The calcined ore is smelted in a huge *blast-furnace* (fig. 246) about fifty or sixty feet high, built of massive masonry, and lined internally with fire-brick. Since it would be impossible to obtain a sufficiently high temperature with the natural draught of this furnace, air is forced into it at the bottom, under a pressure of three or four pounds upon the inch, through three *tuyère* pipes, the nozzles of which pass through apertures in three sides of the furnace.

It would be very easy to reduce to the metallic state the oxide of iron contained in the calcined ore, by simply throwing it into this furnace, together with a proper quantity of coal, coke, or charcoal; but the metallic iron fuses with so great difficulty, that it is impossible to separate it from the clay unless this latter is brought into a liquid state; and even then, the fusion of the iron, which is necessary for complete separation, is only effected after it has formed a more easily fusible compound with a small proportion of carbon derived from the fuel.

Now, clay is even more difficult to fuse than iron, so that it is necessary to add, in the smelting of the ore, some substance capable of forming with the clay a combination which is fusible at the temperature of the furnace. If clay (silicate of alumina) be mixed with limestone (carbonate of lime), and exposed to a high temperature, the carbonic acid is expelled from the limestone, and the lime unites with the clay, forming a double silicate of alumina and lime, which becomes perfectly liquid, and when cool, solidifies to a glass or *slag*. The limestone is here said to act as a *flux*, because it induces the clay to *flow* in the liquid state. In order, therefore, that the clay may be readily separated from the metallic iron,

the calcined ore is mixed with a certain proportion of limestone before being introduced into the furnace.

Great care is necessary in first lighting the blast-furnace lest the new masonry should be cracked by too sudden a rise of temperature, and when once lighted, the furnace is kept in constant work for years until in want of repair. When the fire has been lighted, the furnace is filled up with coke,



Fig. 246. –Blast-furnace for smelting iron ores.

and as soon as this has burnt down to some distance below the chimney, a layer of the mixture of calcined ore with the requisite proportion of limestone is thrown upon it; over this there is placed another layer of coke, then a second layer of the mixture of ore and flux, and so on, in alternate layers, until the furnace has been filled up; when the layers sink down, fresh quantities of fuel, ore, and flux are added, so that the furnace is kept constantly full. As the air passes from the tuyère pipes into the bottom of the furnace, it parts with its oxygen to the carbon of the fuel, which it converts into carbonic acid (CO_2); the latter, passing over the red-hot fuel as it ascends in the furnace, is converted into carbonic oxide (CO) by combining with an additional quantity of carbon. It is this carbonic oxide which reduces the calcined ore to the metallic state, when it comes in contact with it, at a red heat, in the upper part of the furnace, for carbonic oxide removes the oxygen, at a high temperature, from the oxides of iron, and becomes carbonic acid, the iron being left in the metallic state. But the iron so reduced remains disseminated through the mass

of ore until it has passed down to a part of the furnace which is more strongly heated, where the iron enters into combination with a small proportion of carbon to form cast-iron, which fuses and runs down into the *crucible* or cavity for its reception at the bottom of the furnace. At the same time, the clay contained in the ore is acted upon by the lime of the flux, producing a double silicate of alumina and lime, which also falls in the liquid state into the crucible, where it forms a layer of "slag" above the heavier metal. This slag, which has five or six times the bulk of the iron, is allowed to accumulate in the crucible, and to run over its edge down the incline upon which the blast-furnace is built; but when a sufficient quantity of cast-iron has collected at the bottom of the crucible, it is run out through a hole provided for the purpose, either into channels made in a bed of sand, or into iron moulds, where it is cast into rough semi-cylindrical masses called *pigs*, whence cast-iron is also spoken of as *pig-iron*. The temperature of the furnace is, of course, highest in the immediate neighbourhood of the tuyères; the reduction of the iron to the metallic state appears to commence at about two-thirds of the way down the furnace, the volatile matters of the ore, fuel, and flux being driven off before this point is reached.

Some idea may be formed of the immense scale upon which the smelting of iron ores is carried out, when it is stated that each furnace consumes, in the course of twenty-four hours, about 50 tons of coal, 30 tons of ore, 6 tons of limestone, and 100 tons of air. The cast-iron is run off from the crucible once or twice in twelve hours, in quantities of five or six tons at a time. The average yield of calcined clay iron-stone is 35 per cent. of iron.

The gases escaping from the chimney of the blast-furnace are highly inflammable, for they contain, beside the nitrogen of the air blown into the furnace, a considerable quantity of carbonic oxide and some hydrogen, together with the carbonic acid formed by the action of the carbonic oxide upon the ore. Since the carbonic oxide and hydrogen confer considerable heating power upon these gases, they are employed in some iron-works for heating steam-boilers, or for calcining the ore, or for raising the temperature of the blast.

The composition of the gas issuing from a hot-blast furnace (fed with uncoked coal) may be judged of from the following table:—

Gas from Blast-Furnace.

Nitrogen,	55·35 vols.
Carbonic oxide,	25·97 ,,
Hydrogen,	6·73 ,,
Carbonic acid,	7·77 ,,
Marsh-gas,	3·75 ,,
Olefiant-gas,	0·43 ,,
	100·00 ,,

The carbonic oxide, of course, renders these gases highly poisonous, and fatal accidents occasionally happen from this cause.

Although the bulk of the nitrogen present in the air escapes unchanged from the furnace, it is not improbable that a portion of it contributes to the formation of the cyanide of potassium (KCN), which is produced in the lower part of the furnace, the potassium being furnished by the ashes of the fuel.

The hot-blast.—On considering the enormous quantity of air which passes through the blast furnace, it will be seen that it occasions the loss of a considerable amount of heat. In order to economise the fuel, hot-

blast furnaces are fed with air of which the temperature is raised to about 600° F., by passing it through heated iron pipes before allowing it to enter the blast furnace. The higher temperature which is thus attained permits the use of uncoked coal, which would not have given enough heat in a cold-blast furnace, and the same quantity of ore may be smelted with less than half the coal formerly employed. It appears, however, that the *hot-blast iron* is inferior in quality to that obtained from the same ore in a cold-blast furnace, and this is generally explained by referring to the larger quantity of sulphur contained in the raw coal; to the circumstance, that the cast-iron being exposed to a much higher temperature in the hot-blast furnace is more liable to receive and retain a larger amount of foreign substances; and (most important of all) to the custom of extracting iron in a hot-blast furnace from slags obtained in the subsequent processes of the iron-manufacture, which could not be smelted in a cold-blast furnace. These slags always contain sulphur and phosphorus, and therefore yield an inferior quality of iron. Hence the distinction commonly drawn between *mine-iron* extracted from the ore without admixture of slags, and *cinder-iron* in the preparation of which slag or cinder has been employed.

The *slag from the blast-furnace* is essentially a glass composed of a double silicate of alumina and lime, the composition of which varies much according to the nature of the earthy matters in the ore, and the composition of the flux. Its colour is generally opaque white, streaked with blue, green, or brown.

The nature of the flux employed must, of course, be modified according to the composition of the earthy substances (or *gangue*) present in the ore. Where this consists of clay (silicate of alumina) the addition of lime (which is sometimes added in the form of limestone and sometimes as quick-lime) will provide for the formation of the double silicate of alumina and lime. But if the iron-ore happened already to contain limestone, an addition of clay would be necessary, or if quartz were present, consisting of silica only, both lime and alumina (in the form of clay) will be necessary as a flux. It is sometimes found economical to employ a mixture of ores containing different kinds of gangue, so that one may serve as a flux to the other. If a proper proportion of lime were not added, a portion of the oxide of iron would combine with the silica and be carried off in the slag, but if too large a quantity of lime be employed, it will diminish the fusibility of the slag, and prevent the complete separation of the iron from the earthy matter. The most easily fusible slag which can be formed by the action of lime upon clay has the composition $6CaO.Al_2O_3.9SiO_2$; but, in English furnaces, where coal and coke are employed, it is found necessary to employ a larger proportion of lime to convert the sulphur of the fuel into sulphide of calcium, so that the slag commonly has a composition more nearly represented by the formula, $12CaO.2Al_2O_3.9SiO_2$, which would express a compound of 6 molecules of normal silicate of lime with 1 molecule of normal silicate of alumina, $6(2CaO.SiO_2), 2Al_2O_3.3SiO_2$, silicic acid being considered a bibasic acid.

Since iron, manganese, and magnesium are commonly found occupying the place of a portion of the calcium, a more general formula for the slag from English blast furnaces would be—



$$6(2[CaFeMnMg]O.SiO_2), 2Al_2O_3.3SiO_2.$$

A fair impression of the ordinary composition of the slag from blast furnaces is conveyed by the following table :—

Slag from Blast Furnace.

Silica,	43·07
Alumina,	14·85
Lime,	28·92
Magnesia,	5·87
Oxide of iron (FeO),	2·35
Oxide of manganese (MnO),	1·37
Potash,	1·84
Sulphide of calcium,	1·90
Phosphoric acid,	trace
	100·35

These slags are sometimes run from the blast furnace into iron moulds, in which they are cast into blocks for rough building purposes. The presence of a considerable proportion of potash has led to experiments upon their employment as a manure, for which purpose they have been blown out, when liquid, into a finely divided frothy condition fit for grinding and applying to the soil.

214. Cast-Iron is, essentially, composed of iron with from 2 to 5 per cent. of carbon, but always contains other substances derived either from the ore or from the fuel employed in smelting it. On taking into consideration the energetic deoxidising action in the blast furnace, it is not surprising that portions of the various oxygen compounds exposed to it should part with their oxygen, and that the elements thus liberated should find their way into the cast-iron. In this way the silicic acid is reduced, and its silicon is found in cast-iron in quantity sometimes amounting to 3 or 4 per cent. Sulphur and phosphorus are also generally present in cast-iron, but in very much smaller quantity; their presence diminishes its tenacity, and the smelter endeavours to exclude them as far as possible, though a small quantity of phosphorus appears to be rather advantageous for some castings, since it augments the fusibility and fluidity of the cast-iron. The sulphur is chiefly derived from the coal or coke employed in smelting, and for this reason charcoal would be preferable to any other fuel if it could be obtained at a sufficiently cheap rate. The iron-works of America and those of the European continent enjoy a great advantage in this respect over those of England. The phosphorus is obtained chiefly from the phosphoric acid existing in the ore or in the flux. Manganese, amounting to 1 or 2 per cent., is often met with in cast-iron, having been reduced from the oxide of manganese, which is generally found in iron ores. Other metals, such as chromium, cobalt, &c., are also occasionally present, though in so small quantities as to be of no importance in practice.

The following table exhibits the largest and smallest proportions of the various elements determined in the analysis of upwards of a hundred specimens of cast-iron :—

*Composition of Cast-iron.**

	Maximum.	Minimum.	
Carbon,	4·81	1·04	per cent.
Silicon,	4·77	0·08	,,
Sulphur,	1·06	0·00	,,
Phosphorus,	1·87	trace	,,
Manganese,	6·08	trace	,,
Iron,	...	...	

* Compiled from "Percy on Iron and Steel."

In order to understand the difference observed in the several varieties of cast-iron, it is necessary to consider the peculiar relations between iron and carbon. Iron fused in contact with carbon is capable of combining with nearly 6 per cent. of that element, to form a white, brilliant, and brittle compound, which may be represented pretty nearly as composed of Fe_4C. Under certain circumstances, as this compound of iron and carbon cools, a portion of the carbon separates from the iron, and remains disseminated throughout the mass in the form of minute crystalline particles very much resembling natural graphite. If a broken piece of iron containing these scales be examined, the fracture will be found to exhibit a more or less dark grey colour, due to the presence of the uncombined carbon, and for this reason a cast-iron in which a portion of the carbon has thus separated is commonly spoken of as *grey iron*, whilst that in which the whole of the carbon has remained in combination with the metal, exhibits a white fracture, and is termed *white iron* or *bright iron*. Intermediate between these is the variety known as *mottled iron*, which has the appearance of a mixture of the grey and white varieties.

The different condition of the carbon in the two varieties of cast-iron is rendered apparent when the metal is dissolved in diluted sulphuric or hydrochloric acid, for any carbon which exists in the uncombined state will then be left, whilst that which had been in combination with the iron passes off in the form of peculiar compounds of carbon and hydrogen, which impart the disagreeable odour perceived in the gas evolved when the metal is dissolved in an acid.

The properties of these two varieties of cast-iron are widely different, grey iron being so soft that it may be turned in a lathe, whilst the white iron is extremely hard, and of higher specific gravity. Again, although white iron fuses at a lower temperature than grey iron, the latter is far more liquid when fused, and is therefore much better fitted for casting.

Although the presence of uncombined carbon is the chief point which distinguishes grey from white iron, other differences are commonly observed in the composition of the two varieties. The white iron usually contains less silicon than grey iron, but a larger proportion of sulphur. White iron also usually contains a much larger quantity of manganese.

The difference in the composition of these three varieties of cast-iron is shown in the following table:—

	Grey.	Mottled.	White.
Iron,	90·24	89·31	89·86
Combined carbon,	1·02	1·79	2·46
Graphite,	2·64	1·11	0·87
Silicon,	3·06	2·17	1·12
Sulphur,	1·14	1·48	2·52
Phosphorus,	0·93	1·17	0·91
Manganese,	0·83	1·60	2·72
	99·86	98·63	100·46

As might be expected, it is not easy to tell where a cast-iron ceases to be grey and begins to be mottled, or where the mottled iron ends and

white iron begins. There are, in fact, eight varieties of cast-iron in commerce, distinguished by the numbers one to eight, of which No. 1 is dark grey, and contains the largest proportion of graphite, which diminishes in the succeeding numbers up to No. 8, which is the whitest iron, the intermediate numbers being more or less mottled.

The particular variety of cast-iron produced is to some extent under the control of the smelter, a furnace in good order appearing usually to yield grey iron, whilst a defective furnace, or one supplied with too small a proportion of fuel, will commonly give a white iron. But the metal sometimes varies considerably at different levels in the *crucible* of the furnace, so that pigs of different degrees of greyness are obtained at the same tapping.

Mottled cast-iron surpasses both the other varieties in tenacity, and is therefore preferred for such purposes as casting ordnance, where this quality is particularly desirable.

The dark grey iron used for casting, known as *foundry-iron*, is produced at a higher temperature, by supplying the blast furnace with a larger proportion of fuel than is employed in making the lighter *forge-iron* destined for conversion into wrought-iron. The extra consumption of fuel, of course, renders the foundry-iron more expensive. When a furnace is worked with a low charge of fuel to produce a white iron, a larger quantity of iron is lost in the slag, sometimes amounting to 5 per cent. of the metal, whilst the average loss in producing grey iron does not exceed 2 per cent. Ores containing a large proportion of manganese are generally found to yield a white iron.

When grey iron is melted, the particles of graphite to which its grey colour is due are dissolved by the liquid iron, and if it be poured into a cold iron mould so as to solidify it as rapidly as possible, the external portion of the casting will present much of the hardness and appearance of white iron, the sudden cooling having prevented the separation of the graphite. This affords the explanation of the process of *chill-casting*, by which shot, &c., made of the soft fusible grey iron, are made to acquire externally a hardness approaching that of steel.

The *specific gravity* of cast-iron varies between 6·92 (grey) and 7·53 (white), and its *fusing point* is somewhat below 3000° F.

Conversion of Cast-Iron into Bar or Wrought Iron.

215. In order to convert cast-iron into bar-iron, it is necessary to reduce it as far as possible to the condition of pure iron, by removing the carbon, silicon, and other substances associated with it. This purification is effected upon the principle, that when cast-iron is strongly heated in contact with oxide of iron, its carbon is evolved in the form of carbonic oxide, whilst the silicon, also combining with the oxygen from a part of the oxide of iron, is converted into silicic acid, which unites with another portion of oxide to form a fusible slag easily separated from the metal.

The most important of the processes employed for the conversion of pig-iron into bar-iron, is that known as the *puddling* process, but this is sometimes preceded by the process of *refining*, which will therefore be first described.

Refining cast-iron.—This process consists essentially in exposing the

metal, in a fused state, to the action of a blast of air. The *refinery* (figs. 247, 248) is a rectangular trough with double walls of cast-iron, between which cold water is kept circulating to prevent their fusion. This trough is about $3\frac{1}{2}$ feet long by $2\frac{1}{2}$ wide, and usually lined with fire-clay; on each side of it are arranged three tuyère pipes for the supply of air, inclined at an angle of 25° to 30° to the bottom of the furnace, which is fed with coke, unless the very best iron is required, as for the manufacture of tin-plate, when charcoal is generally used in the refinery.

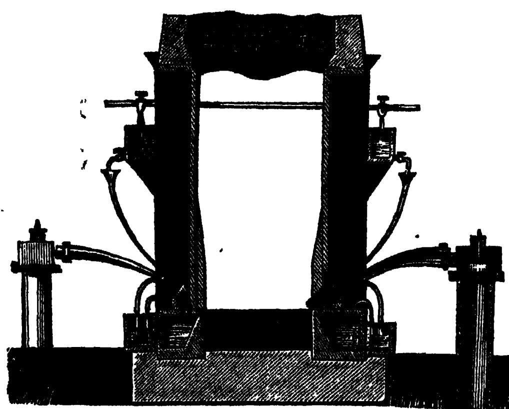


Fig. 247.—Hearth for refining pig-iron.

This furnace having been filled to a certain height with fuel, five or six pigs of iron (from 20 to 30 cwt.) are arranged symmetrically upon it, and covered with coke, a blast of air being forced in through the tuyères, under a pressure of about 3 lbs. upon the inch. In about a quarter of an hour the metal begins to fuse gradually, and to trickle down through the fuel to the bottom of the refinery, a portion of the iron being converted into oxide in its descent, by the air issuing from the tuyère pipes. When the whole of the metal has been fused, the air is still allowed to play for some time upon its surface, when the fused metal appears to boil in consequence of the escape of bubbles of carbonic oxide.

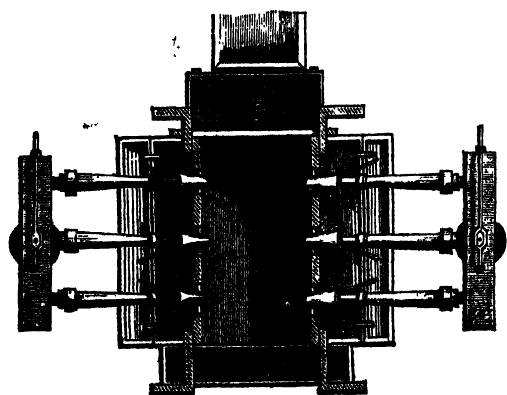


Fig. 248.—Hearth for refining pig-iron.

After about two hours the tap hole is opened, and the molten metal run out into a flat cast-iron mould kept cold by water, in order to chill the metal and render it brittle. The plate of *refined iron* thus obtained is usually about 2 inches thick. The slag (or *finery cinder*) is generally received in a separate mould; its composition may be generally expressed by the formula $2FeO.SiO_2$, the silicic acid having been derived from the silicon contained in the cast-iron.

The change effected in the composition of the iron by the process of refining will be apparent from the following table:—

Refined Iron.

Iron,	95·14
Carbon,	3·07
Silicon,	0·63
Sulphur,	0·16
Phosphorus,	0·73
Manganese,	trace
Slag,	0·44
	100·17

The carbon, therefore, is not nearly so much diminished as the silicon, which is in some cases reduced to $\frac{1}{10}$th of its former proportion by the refining process. Half of the sulphur is also sometimes removed, being found in the slag as sulphide of iron. The phosphorus is not removed to the same extent in the refining process, though some of it is converted into phosphoric acid, which may be found in the finery cinder.

The further purification of the metal could not be effected in the refinery, since the fusibility of the iron is so greatly diminished as it approaches to a pure state, that it could not be retained in a fluid condition at the temperature attainable in this furnace, and a more spacious hearth is required upon which the pasty metal may be kneaded into close contact with the oxide of iron which is to complete the oxidation and separation of the carbon. For this reason the metal is transferred to the puddling furnace.

The *puddling* process is carried out in a reverberatory furnace (figs. 249, 250) connected with a tall chimney provided with a damper, so as to admit of a very perfect regulation of the draught. A bridge of fire-brick between

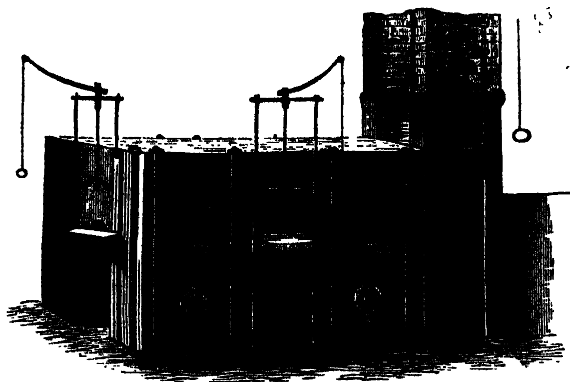


Fig. 249.—Puddling furnace.

the grate and the hearth prevents the contact of the coal with the iron to be puddled. The hearth is composed either of fire-brick or of cast-iron plates, covered with a layer of very infusible slag, and cooled by a free circulation of air beneath them. This hearth is about 6 feet in length, by 4 feet in the widest part near the grate, and 2 feet at the opposite end; it is slightly inclined towards the end farthest from the grate, and finishes in a very considerable slope, at the lowest point of which is the *floss-hole* for the removal of the slag. Since the metal is to attain a very high temperature in this furnace (estimated at 3000° F.), it is usually covered

with an iron casing, so as to prevent any entrance of cold air through chinks in the brick work.

About 5 cwt. of the fine metal is broken up and heaped upon the hearth of this furnace, together with about 1 cwt. of iron scales (black

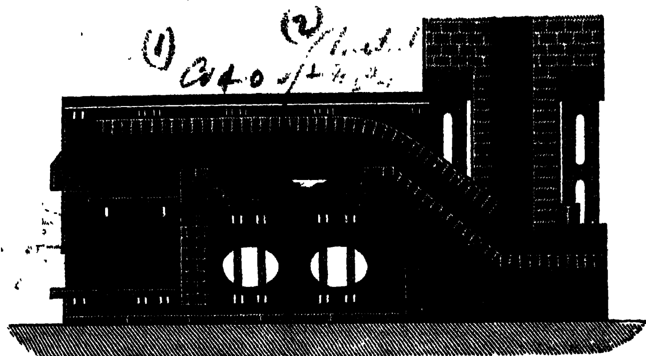


Fig. 250.—Puddling furnace.

oxide of iron, Fe_3O_4), and of *hammer-slag* (basic silicate of iron, obtained in subsequent operations), which are added in order to assist in oxidising the impurities. When the metal has fused, the mass is well stirred or puddled, so that the oxide of iron may be brought into contact with every part of the metal, to effect the oxidation of the impurities. The metal now appears to boil, in consequence of the escape of carbonic oxide, and in about an hour from the commencement of the puddling, so much of the carbon has been removed that the fusibility of the metal is considerably diminished, and instead of retaining a fused condition at the temperature prevailing in the furnace, it assumes a granular, *sandy*, or *dry* state, spongy masses of pure iron separating or *coming to nature* in the fused mass. The puddling of the iron is continued until the whole has assumed this granular appearance, when the evolution of carbonic oxide ceases almost entirely, showing that the removal of the carbon is nearly completed. The damper is now gradually raised, so as to increase the temperature and soften the particles of iron, in order that they may be collected into a mass; and the more easily to effect this, a part of the slag is run off through the floss-hole. The workman then collects some of the iron upon the end of the paddle, and rolls it about on the hearth until he has collected a sort of rough ball of iron, weighing about half-a-hundred weight. When all the iron has been collected into balls in this way, they are placed in the hottest part of the furnace, and pressed occasionally with the paddle, so as to squeeze out a portion of the slag with which their interstices are filled. The doors are then closed to raise the interior of the furnace to a very high temperature, and after a short time, when the balls are sufficiently heated, they are removed from the furnace, and placed under a steam hammer, which squeezes out the liquid slag, and forces the softened particles of iron to cohere into a continuous oblong mass or *bloom*, which is then passed between rollers by which it is extended into bars. These bars, however (*Rough* or *Puddled*, or *No.* 1 *Bar*), are always hard and brittle, and are only fit for such constructions as railway bars, where hardness is required rather than great tenacity. In order to improve this latter quality, the rough bars are cut up into short lengths,

which are made into bundles, and after being raised to a high temperature in the *mill-furnace*, are passed through rollers, which weld the several bars into one compound bar, to be subsequently passed through other rollers until it has acquired the desired dimensions. By thus *fagotting* or *piling* the bars, their texture is rendered far more uniform, and they are made to assume a fibrous structure, which greatly increases their strength (*Merchant Bar*, or *No. 2 Bar*). To obtain the best, or *No. 3 Bar*, or *wire-iron*, these bars are doubled upon themselves, raised to a welding heat, and again passed between rollers. These repeated rollings have the effect of thoroughly squeezing out the slag which is mechanically entangled among the particles of iron in the rough bars, and would produce flaws if allowed to remain in the metal. A slight improvement appears also to be effected in the chemical composition of the iron during the rolling, some of the carbon, silicon, phosphorus, and sulphur, still retained by the puddled iron, becoming oxidised, and passing away as carbonic oxide and slag.

The following table exhibits the change in chemical composition which takes place in pig-iron when puddled (without previous refining) and rolled into wire-iron :—

Effect of Puddling and Forging on Cast-iron.

In 100 parts.	Carbon.	Silicon.	Sulphur.	Phosphorus.
Grey pig-iron,	2·275	2·720	0·301	0·645
Puddled bar,	0·296	0·120	0·134	0·139
Wire-iron,	0·111	0·088	0·094	0·117

About 90 parts of bar-iron are obtained from 100 of refined iron by the puddling process, the difference representing the carbon which has passed off as carbonic oxide, and the silicon, sulphur, phosphorus, and iron, which have been removed in the slag, or *tap-cinder*, this being essentially a silicate of protoxide and sesquioxide of iron, varying much in composition according to the character of the iron employed for puddling, and the proportions of iron-scale and hammer-slag introduced into the furnace. Of course, also, the material of which the hearth is composed will influence the composition of the slag. The following table affords an illustration of its composition :—

Tap-Cinder from Puddling Furnace.

Protoxide of iron (FeO),	57·67
Peroxide of iron (Fe_2O_3),	13·53
Silicic acid,	8·32
Phosphoric acid,	7·29
Sulphide of iron,	7·07
Lime,	4·70
Oxide of manganese,	0·78
Magnesia,	0·26
	99·62

The lime in the above cinder was probably derived from the hearth of the furnace, which is sometimes lined with that material to assist in removing the sulphur.

When pig-iron is puddled without undergoing the refining process, it becomes much more liquid than refined iron, and the process is sometimes described as the *boiling process*, whilst refined iron undergoes *dry puddling*.

It will be observed that this process of puddling is attended with some important disadvantages; it involves a great expenditure of manual labour, and of a most exhausting kind; the very high temperature to which the puddler is exposed renders him liable to lung disease, and cataract is not uncommonly caused by the intense light from the glowing iron; the wear and tear of the puddling furnace is very considerable, and since it receives only ten or eleven charges of about five cwts. each in the course of twenty-four hours, it is necessary to work five or six puddling furnaces at once, in order to convert into bar-iron the whole of the cast-iron turned out from a single blast furnace. These considerations have led to several attempts to improve the puddling process by employing revolving furnaces and other mechanical arrangements to supersede the heavy manual labour, and even to dispense with it altogether by forcing the air into the molten iron. The most generally known of the processes devised for this purpose is that of Bessemer, which consists in running the melted cast-iron into a huge crucible, and forcing air up through it under considerable pressure, thus combining the purifying influence of the blast of air in the refinery with the mechanical agitation effected in the puddling furnace. Bessemer's *converting vessel* (fig 251) is a large, nearly cylindrical crucible of wrought iron, lined with fire-clay, having apertures (A) at the bottom, through which air is blown at a pressure of fifteen or twenty pounds upon the inch. This vessel is sometimes large enough to receive ten tons of cast-iron for a charge. The metal having been melted in a separate furnace, is run into the converting vessel, the blast being already turned on so that the liquid iron may not run into the air tubes. The iron burns vividly, and the oxide of iron produced is diffused in a melted state through the mass of metal by the rapid current of air. This oxide of iron acts upon the silicon and carbon in the cast-iron, converting the latter into carbonic oxide, which burns with flame at the mouth of the converter, and the former into silicic acid, which enters into the slag, and is carried up as a froth to the surface of the liquid iron. The blast of air or *blow* is continued for about twenty minutes, when the disappearance of the flame of carbonic oxide indicates the completion of the process; but the remaining purified iron is not pasty, as in the puddling furnace, being retained in a perfectly liquid condition by the high temperature resulting from the combustion of part of the iron, so that the metal may be run out into moulds by tilting the converting vessel, which is usually hung upon trunnions. In this way about 85 parts of bar-iron are obtained from 100 of pig-iron.

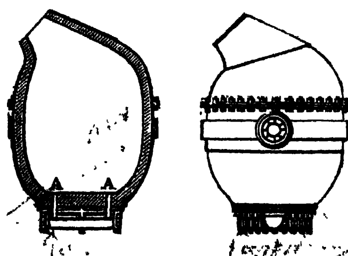


Fig. 251.—Bessemer's converting vessel.

Although so great an economy of time and labour would result from the application of Bessemer's process, it has not superseded the puddling process, because it does not remove the sulphur and phosphorus from the pig-iron, so that only the best varieties of that material, extracted from

hæmatite or magnetic ore, yield a bar-iron of good quality when purified in this way. Moreover, the process is applicable only to grey iron rich in carbon and silicon, which is more expensive than the light forge irons treated in the puddling furnace. Its application to the manufacture of steel will be noticed hereafter. The effect of the Bessemer process upon a particular specimen of pig-iron is shown in the table—

In 100 parts of Pig-iron.	Before.	After.
Carbon,	3·309	0·218
Silicon,	0·595	none
Sulphur,	0·485	0·402
Phosphorus,	1·012	1·102

Composition of bar-iron.—Even the best bar-iron contains from 0·1 to 0·3 per cent. of carbon, together with minute proportions of silicon, sulphur, and phosphorus. Perfectly pure iron is inferior in hardness and tenacity to that which contains a small proportion of carbon.

Bar-iron is liable to two important defects, which are technically known as *cold-shortness* and *red-shortness*. Cold-short iron is brittle at ordinary temperatures, and appears to owe this to the presence of phosphorus, of which element 0·5 per cent. is sufficient materially to diminish the tenacity of the iron. When the iron is liable to brittleness at a red heat, it is termed red-short iron, and a very little sulphur is sufficient to affect the quality of the iron in this respect.

There is much difference of opinion as to the true causes of the variation in the strength of wrought-iron, and this is not surprising when we reflect upon the number of circumstances which may be reasonally expected to exert some influence upon it. Not only the proportions of carbon, silicon, sulphur, phosphorus, and manganese may be supposed to affect the quality of the iron, but the state of combination in which these elements exist in the mass is not unlikely to cause a difference. It also appears certain that the mechanical structure, dependent upon the arrangement of the particles composing the mass of metal, has at least as much influence upon the tenacity of the iron as its chemical composition.

The best bar-iron, if broken slowly, always exhibits a fibrous structure, the particles of iron being arranged in parallel lines. This appears to contribute greatly to the strength of the iron, for when it is wanting, and the bar is composed of a confused mass of crystals, it is weaker in proportion to the size of the crystals. The presence of phosphorus is said to favour the formation of large crystals, and hence to produce cold-shortness. There is some reason to believe that the fibrous is sometimes exchanged for the crystalline texture under the influence of frequent vibrations, as in the case of railway axles, girders of suspension-bridges, &c.

Considering the difficult fusibility of bar-iron, it is fortunate that it possesses the property of being *welded*, that is, of being united by hammering when softened by heat. It is customary first to sprinkle the heated bars with sand or clay in order to convert the superficial oxide of iron into a liquid silicate, which will be forced out from between them by hammering or rolling, leaving the clean metallic surfaces to adhere. *Burnt iron* does not weld, and is largely crystalline in structure.

Manufacture of Steel.

216. Steel differs from bar-iron in possessing the property of becoming very hard and brittle when heated to redness and then suddenly cooled by being plunged into water. Perfectly pure iron, obtained by the electrotype process, is not hardened by sudden cooling; but all bar-iron which contains carbon does exhibit this property in a greater or less degree according to the proportion of carbon present. It does not become decidedly steely, however, until the carbon amounts to 0·3 per cent. The hardest steel contains about 1·2 per cent. of carbon, and when the proportion reaches 1·4 per cent. it begins to assume the properties of white cast-iron. Bar-iron may, therefore, be converted into steel by the addition of about one per cent. of carbon, and, conversely, cast-iron is converted into steel when the quantity of carbon contained in it is reduced to that amount. There are thus two processes by which steel may be produced; but that which is employed almost exclusively in this country consists in combining bar-iron with the requisite amount of carbon by what is technically known as *cementation*, the bars being imbedded in charcoal and exposed for several days to a high temperature.

The operation is effected in large chests of fire-brick or stone, about 10 or 12 feet long by 3 feet wide and 3 feet deep.

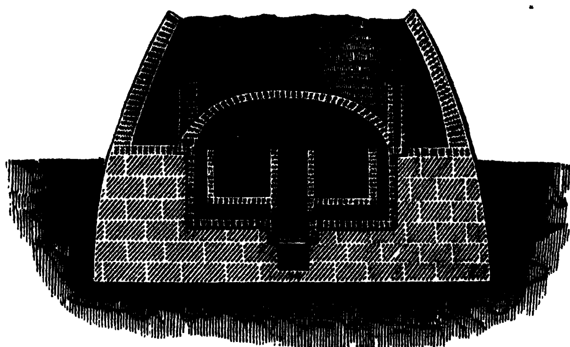


Fig. 252.—Furnace for converting bar-iron into steel.

Two of these chests are built into a dome-shaped furnace (*converting furnace*, fig. 252), so that the flame may circulate round them, and the furnace is surrounded with a conical jacket of brick-work in order to allow a steady temperature to be maintained in it for some days. The charcoal is ground so as to pass through a sieve of $\frac{1}{4}$ inch mesh, and spread in an even layer upon the bottom of the chests. Upon this the bars of iron, which must be of the best quality, are laid in regular order, a small interval being left between them, which is afterwards filled in with the charcoal powder, with a layer of which the bars are now covered; over this more bars are laid, then another layer of charcoal, and so on until the chest is filled. Each chest holds 5 or 6 tons of bars. One of the bars is allowed to project through an opening in the end of the chest, so that the workmen may withdraw it from time to time and judge of the progress of the operation. The whole is covered in with a layer of about 6 inches of damp clay or sand.

The fire is carefully and gradually lighted, lest the chests should be split by too sudden application of heat, and the temperature is eventually raised to about the fusing point of copper (2000° F.), at which it is maintained for a period varying with the quality of steel which it is desired to obtain. Six or eight days suffice to produce steel of moderate hardness; but the process is continued for three or four days longer if very hard steel be required. The fire is gradually extinguished, so that the chests are about ten days in cooling down.

On opening the chests, the bars are found to have suffered a remarkable change both in their external appearance and internal structure. They are covered with large blisters, obviously produced by some gaseous substance raising the softened surface of the metal in its attempt to escape. It is conjectured either that the small quantity of sulphur present in the bar-iron is converted into bisulphide of carbon during the cementation process, and that the vapour of this substance swells the softened metal into bubbles as it passes of; or that the blisters are caused by carbonic oxide produced by the action of the carbon upon particles of slag accidentally present in the bar. On breaking the bars across, the fracture is found to have a finely granular structure, instead of the fibrous appearance exhibited by bar-iron. Chemical analysis shows that the iron has combined with about one per cent. of carbon, and the most remarkable part of the result is that this carbon is not only found in the external layer of iron, which has been in direct contact with the heated charcoal, but is also present in the very centre of the bar. It is this transmission of the solid carbon through the solid mass of iron which is implied by the term *cementation*. The chemistry of the process probably consists in the formation of carbonic oxide from the small quantity of atmospheric oxygen in the chest, and the removal of one-half of the carbon from this carbonic oxide, by the iron, which it converts into steel, leaving carbonic acid ($2CO - C = CO_2$) to be reconverted into carbonic oxide by taking up more carbon from the charcoal ($CO_2 + C = CO$), which it transfers again to the iron. Experiment has recently shown that soft iron is capable of absorbing, mechanically, 4·15 volumes of carbonic oxide at a low red heat, so that the action of the gas upon the metal may occur throughout the substance of the bar. The carbonic oxide is retained unaltered by the iron, after cooling, unless the bar is raised to the temperature required for the production of steel.

The *blistered steel* obtained by this process is, as would be expected, far from uniform either in composition or in texture; some portions of the bar contain more carbon than others, and the interior contains numerous cavities. In order to improve its quality, it is subjected to a process of fagotting similar to that mentioned in the case of bar-iron; the bars of blistered steel, being cut into short lengths, are made up into bundles, which are raised to a welding heat, and placed under a tilt-hammer weighing about 2 cwt., which strikes two or three hundred blows in a minute; in this way, the several bars are consolidated into one compound bar, which is then extended under the hammer till of the required dimensions. The bars, before being hammered, are sprinkled with sand, which combines with the oxide of iron upon the surface, and forms a vitreous layer which protects the bar from further oxidation. The steel which has been thus hammered is much denser and more uniform in composition; its tenacity, malleability, and ductility are greatly increased, and it is fitted for the manufacture of shears, files, and other

tools. It is commonly known as *shear steel.* Double shear steel is obtained by breaking the tilted bars in two, and welding these into a compound bar.

The best variety of steel, however, which is perfectly homogeneous in composition, is that known as *cast steel,* to obtain which, about 30 lbs. of blistered steel are broken into fragments, and fused in a fire-clay or plumbago crucible, heated in a wind-furnace, the surface of the metal being protected from oxidation by a little glass melted upon it. The fused steel is cast into ingots, several crucibles being emptied simultaneously into the same mould. Cast steel is far superior in density and hardness to shear steel, but since it is exceedingly brittle at a red heat, great care is necessary in forging it. It has been found that the addition, to 100 parts of the cast steel, of one part of a mixture of charcoal and oxide of manganese, produces a very fine grained steel which admits of being cast on to a bar of wrought-iron in the ingot-mould, so that the tenacity of the latter may compensate for the brittleness of the steel when the compound bar is forged, the wrought-iron forming the back of the implement, and the steel its cutting edge.

This addition of manganese to the cast steel (Heath's patent) has effected a great reduction in its cost, allowing the use of blister steel made from British bar-iron, whereas, before its introduction, only the expensive iron of Swedish or Russian make could be employed. Only traces of manganese pass into the steel, the bulk of it going into the slag, and apparently, carrying the sulphur and phosphorus with it.

After the steel has been forged into the shape of any implement, it is hardened by being heated to redness, and suddenly chilled in cold water, or oil, or mercury. It can thus be rendered nearly as hard as diamond, at the same time increasing slightly in volume (sp. gr. of cast steel 7·93 ; after hardening, 7·66). The chemical difference between hard and soft steel appears to be of the same kind as that between grey and white cast-iron (p. 306), the great proportion of the carbon in hard steel being in combination with the metal, while in soft steel the greater part seems to be in intimate mechanical admixture with the iron, for it is left undissolved on treating the steel with an acid. If the hardened steel be heated to redness, and allowed to cool slowly, it is again converted into soft steel, but by heating it to a temperature short of a red heat, its hardness may be proportionally reduced. This is taken advantage of in annealing the steel or "letting it down" to the proper temper. The very hardest steel is almost as brittle as glass, and totally unfit for any ordinary use, but by heating it to a given temperature and allowing it to cool, its elasticity may be increased to the desired extent, without reducing its hardness below that required for the implement in hand. On heating a steel blade gradually over a flame, it will acquire a light yellow colour when its temperature reaches 430° F., from the formation of a thin film of oxide ; as the temperature rises, the thickness of the film increases, and at 470° a decided yellow colour is seen, which assumes a brown shade at 490°, becomes purple at 520°, and blue at 550°. At a still higher temperature the film of oxide becomes so thick as to be black and opaque. Steel which has been heated to 430°, and allowed to cool slowly, is said to be *tempered to the yellow,* and is hard enough to take a very fine cutting edge, whilst, if *tempered to the blue,* at 550°, it is too soft to take a very keen edge, but has a very high degree of elasticity. The following table indicates the tempering heats for various implements :—

Tempering of Steel.

Temperature, F.	Colour.	Implements thus tempered.
430° to 450°.	Straw-yellow.	Razors, lancets.
470°	Yellow.	Pen-knives.
490°	Brown-yellow.	Large shears for cutting metal.
510°	Brown-purple.	Clasp-knives.
520°	Purple.	Table-knives.
530° to 570°.	Blue.	Watch-springs, sword-blades.

If a knife blade be heated to redness, its *temper is spoilt,* for it is converted into soft steel.

In general, the steel implements are ground after being tempered, so that they are not seen of the colours mentioned above, except in the case of watch-springs.

A steel blade may be easily distinguished from iron by placing a drop of diluted nitric acid upon it, when a dark stain is produced upon the steel, from the separation of the carbon.

Some small instruments, such as keys, gun-locks, &c., which are exposed to considerable wear and tear by friction, and require the external hardness of steel without its brittleness, are forged from bar-iron, and converted externally into steel by the process of *case-hardening,* which consists in heating them in contact with some substance containing carbon (such as bone-dust, yellow prussiate of potash, &c.), and afterwards chilling in water. A process which is the reverse of this is adopted in order to increase the tenacity of stirrups, bits, and similar articles made of cast-iron; by heating them for some hours, in contact with oxide of iron or manganese, their carbon and silicon are removed in the forms of carbonic oxide and silicic acid, and they become converted into *malleable cast-iron.*

The opinion that steel owes its properties entirely to the presence of carbon is not universally entertained. Some chemists believe that nitrogen (or some analogous element) is an indispensable constituent, but the proportion of nitrogen found in steel is too minute to warrant this supposition. Titanium is alleged by some authorities to have an important influence upon the quality of steel, but this also appears to be a doubtful matter. Bar-iron may be converted into steel by being kept at a high temperature in an atmosphere of coal-gas, from which it abstracts carbon.

Bessemer steel was originally produced by arresting the purification of cast-iron in Bessemer's process (page 312), as soon as the carbon had diminished to about one per cent., when the steel was poured out in the fused state, *i.e.,* in the form of cast steel. A steel of better quality, however, has been obtained by continuing the purification until liquid bar-iron remains in the converter, and introducing the proper proportion of carbon in the form of a peculiar description of white cast-iron known as *Spiegel-eisen* (mirror iron), which crystallises in lustrous tabular crystals, and contains large proportions of carbon and manganese, being obtained by smelting spathic iron ore rich in manganese, with charcoal as fuel.

The *Spiegel-eisen* is added, in a melted state, to the Bessemer iron before pouring from the converter.

The composition of a sample of *Spiegel-eisen* smelted from a spathic ore, found near Müsen in Prussia, is here given :—

Spiegel-eisen.

Iron,	82·86
Manganese,	10·71
Silicon,	1·00
Carbon,	4·32
	98·89

Homogeneous iron, as it is called, is really a *mild* steel containing a low percentage of carbon, and obtained by fusing the best Swedish bar-iron with carbonaceous matters. It is remarkable for its malleability and toughness, and, having undergone complete fusion, it is more likely to be homogeneous in composition and structure than wrought-iron produced by puddling.

Puddled steel is obtained by arresting the puddling process at an earlier stage than usual, so as to leave a proportion of carbon varying from 0·3 to 1·0 per cent.

Natural steel or *German steel* results in a similar way, from the incomplete purification of cast-iron in the refinery. The presence of manganese in the iron is favourable to its production.

Krupp's cast steel, manufactured at Essen near Cologne, and employed for ordnance, shells, &c., is a puddled steel made from hæmatite and spathic ore, smelted with coke. The iron thus obtained contains much manganese, which is removed in the puddling process. Krupp's steel contains about 1·2 per cent. of combined carbon, and is fused with a little bar-iron for casting ordnance. The fusion is effected in black lead crucibles holding 30 lbs. each, of which as many as 1200 are emptied simultaneously into the mould for the largest castings. A casting of 16 tons requires about 400 men, who act together in well-disciplined gangs, so that the stream of molten metal shall flow continuously along the gutters into the mould. Such large castings must be allowed to cool very gradually, so that they are kept surrounded with hot cinders, sometimes for two or three months, till required for forging.

217. *Direct extraction of wrought-iron from the ore.*—Where very rich and pure ores of iron, such as hæmatite and magnetic iron ore, are obtainable, and fuel is abundant, the metal is sometimes extracted without being converted into cast-iron. It is probable that the iron of antiquity was extracted in this way, for it is doubtful whether cast-iron was known to the ancients, and the slag left from old iron-works does not indicate the use of any flux. Some works of this description are still in operation in the Pyrenees, where the *Catalan process* is employed. The crucible is lined at the sides with thick iron plates, and at the bottom with a refractory stone. A quantity of red-hot charcoal is thrown into it, and the space above this is temporarily divided into two compartments by a shovel. The compartment nearest to the pipe through which the blast enters is charged with charcoal, and the other compartment with the calcined ore in small pieces. The shovel is then withdrawn, and a gradually increasing current of air supplied, fresh ore and fuel being added

as they sink down. One part of the oxide of iron is reduced to the metallic state by the carbonic oxide, and the rest combines with the silica present in the ore to form a slag. After about five hours the spongy masses of bar-iron are collected into a ball upon the end of an iron rod, and hammered into a compact mass like the metal obtained in the

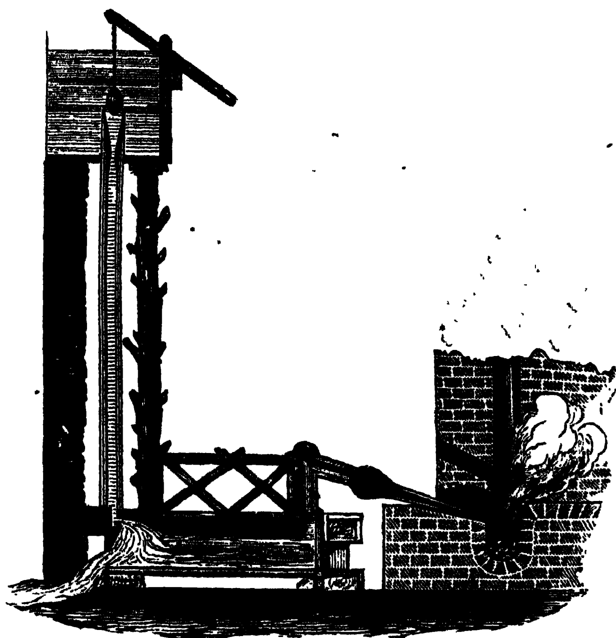


Fig. 253.—Catalan forge for smelting iron ores.

puddling furnace. The blowing machine employed in the Pyrenees is one in which the fall of water from a cistern down a long wooden pipe, sucks in, through lateral apertures, a supply of air, which it carries down with it into a box, from which the pressure of the column of water projects it with some force through the blast-pipe, the water escaping from the box through another aperture.

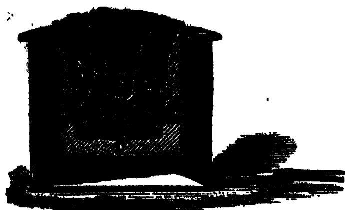
In the North American *bloomery forges* a modernised form of the same process is adopted.

The wrought-iron produced by this process always contains a larger proportion of carbon than puddled iron, and is therefore somewhat steely in character.

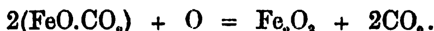
218. *Extraction of iron on the small scale.*—In the laboratory, iron may be extracted from hæmatite in the following manner:—A fire-clay crucible (A, fig. 254), about 3 inches high, is filled with damp charcoal powder, rammed down in successive layers; a smooth conical cavity is scooped in the charcoal, and a mixture of 100 grs. red hæmatite, 25 grs. chalk, and 25 grs. pipe-clay, is introduced into it; the mixture is covered with a layer of charcoal, and a lid placed on the crucible, which is heated in a Sefström blast furnace,* fed with coke in small pieces, for about half

* This very useful furnace, shown in section in fig. 254, consists of two iron cylinders with a space (B) between them, into which air is forced through the tube C by a double-action bellows. The inner cylinder has a fire-clay lining (D), through which four or six copper tubes (E) admit the blast into the fuel.

an hour. On breaking the cold crucible, a button of cast-iron* will be obtained. Nearly pure iron may be prepared by fusing the best wire-iron with about one-fifth of its weight of pure peroxide of iron, to oxidise the carbon and silicon which it contains. Some powdered green glass, perfectly free from lead, must be employed as a flux, and the crucible (with its cover well cemented on with fire-clay) exposed for an hour to a very high temperature. A silvery button of iron will then be obtained.


Fig. 254.—Sefström furnace.

219.—*Chemical properties of iron.*—In its ordinary condition, iron is unaffected by perfectly dry air, but in the presence of moisture it is gradually converted into hydrated sesquioxide of iron ($2Fe_2O_3.3H_2O$), or *rust.* This conversion takes place more rapidly when carbonic acid is present, water being then decomposed, and carbonate of iron formed ($Fe + H_2O + CO_2 = FeO.CO_2 + H_2$); this is dissolved by the carbonic acid present, and the solution rapidly absorbs oxygen from the air depositing the sesquioxide of iron in a hydrated state—



$$2(FeO.CO_2) + O = Fe_2O_3 + 2CO_2.$$

When iron nails are driven into a new oaken fence, a black streak will soon be observed descending from each nail, caused by the formation of tannate of iron (ink) by the action of the tannic acid in the wood upon the solution of carbonate of iron formed from the nails. The diffusion of *iron-mould* stains through the fibre of wet linen by contact with a nail, is also caused by the formation of solution of carbonate of iron. The iron in *chalybeate* waters is also generally present in the form of carbonate dissolved in carbonic acid, and hence the rusty deposit which is formed when they are exposed to the air. Iron does not rust in water containing a free alkali, or alkaline earth, or an alkaline carbonate.

Concentrated sulphuric and nitric acids do not act upon iron at the ordinary temperature, though they dissolve it rapidly when diluted. Even when boiling, strong sulphuric acid acts upon it but slowly. When iron has been immersed in strong nitric acid (sp. gr. 1·45), it is found to be unacted upon when subsequently placed in diluted nitric acid, unless previously wiped; it is then said to have assumed the *passive state.* If iron wire be placed in nitric acid of sp. gr. 1·35, it is acted upon immediately, but if a piece of gold or platinum be made to touch it beneath the acid, the iron assumes the passive state, and the action ceases at once. A state similar to this, the cause of which has not yet been satisfactorily explained, is sometimes assumed by other metals, though in a less marked degree.

220. *Oxides of iron.*—Three compounds of iron with oxygen are known in the separate state, and one is believed to exist in certain compounds—

Protoxide of iron, or ferrous oxide,	FeO
Sesquioxide or peroxide of iron, or ferric oxide,	Fe_2O_3
Magnetic oxide, or ferroso-ferric oxide,	Fe_3O_4
Ferric acid (?),	FeO_3

The *protoxide of iron* is little known in the separate state, on account of the readiness with which it absorbs oxygen and forms sesquioxide of iron. If a little potash or ammonia be added to a solution of the green sulphate

of iron ($FeO.SO_3$), a whitish precipitate of hydrated protoxide of iron is formed, which immediately absorbs oxygen, and is converted into the dingy green hydrate of the magnetic oxide; on exposing this to the air, it absorbs more oxygen and becomes brown hydrated peroxide. This disposition of the hydrated protoxide to absorb oxygen is turned to advantage when a mixture of sulphate of iron with lime or potash is employed for converting blue into white indigo. The protoxide of iron is a strong base.

Peroxide or *red oxide of iron* has been already noticed among the ores of iron, and has also been referred to as occurring in commerce under the names of *colcothar*, *jeweller's rouge*, and *Venetian red*, which are obtained by the calcination of the green sulphate of iron—



$$2(FeO.SO_3) = Fe_2O_3 + SO_2 + SO_3.$$

The hydrated peroxide ($2Fe_2O_3.3H_2O$), obtained by decomposing a solution of perchloride of iron with an alkali, forms a brown gelatinous precipitate, which is easily dissolved by acids; but if it be dried and heated to dull redness, it exhibits a sudden glow, and is converted into a modification which is dissolved with great difficulty by acids, although it has the same composition as the soluble form which has not been strongly heated. When the peroxide of iron is heated to whiteness, it loses oxygen, and is converted into magnetic oxide of iron, $3Fe_2O_3 = 2Fe_3O_4 + O$. Existing as it does in all soils, sesquioxide of iron is believed to fulfil the purpose of oxidising the organic matter in the soil, and converting its carbon into carbonic acid, to be absorbed by the plant; the sesquioxide being thus reduced to protoxide, which is oxidised by the air, and fitted to perform again the same office. The sesquioxide of iron, like alumina, is a weak base, and even exhibits some tendency to play the part of an acid towards strong bases, though not in so marked a degree as alumina.

Magnetic or *black oxide of iron* is generally regarded as a compound of the protoxide with the sesquioxide of iron ($FeO.Fe_2O_3$), a view which is confirmed by the occurrence of a number of minerals having the same crystalline form as the native magnetic oxide of iron, in which the iron, or part of it, is displaced by other metals. Thus, *spinelle* is $MgO.Al_2O_3$; *Franklinite*, $ZnO.Fe_2O_3$; chrome-iron ore, $FeO.Cr_2O_3$. The natural magnetic oxide was mentioned among the ores of iron, and this oxide has been seen to be the result of the action of air or steam upon iron at a high temperature. The hydrated magnetic oxide of iron ($Fe_3O_4.H_2O$) is obtained as a black crystalline powder by mixing one equivalent of protosulphate with one equivalent of persulphate of iron, and pouring the mixture into a slight excess of solution of ammonia, which is afterwards boiled with it. Magnetic oxide of iron, when acted upon by acids, yields mixtures of protosalts and persalts of iron, so that it is not an independent basic oxide.

Ferric acid is only known in combination with bases as *ferrates*. When iron filings are strongly heated with nitre, and the mass treated with a little water, a fine purple solution of ferrate of potash is obtained. A better method of preparing this salt consists in suspending 1 part of freshly precipitated sesquioxide of iron in 50 parts of water, adding 30 parts of solid hydrate of potash, and passing chlorine till a slight effervescence commences; $Fe_2O_3 + Cl_6 + 10KHO = 6KCl + 2(K_2FeO_4) + 5H_2O$; the ferrate of potash forms a black precipitate, being insoluble in the strongly alkaline solution, though it dissolves in pure water to form a purple solution, which is decomposed even by dilution, oxygen escaping, and hydrated peroxide of iron being pre-

cipitated, $2(K_2FeO_4) = 2K_2O + Fe_2O_3 + O_3$. A similar decomposition takes place on boiling a strong solution, or on adding an acid with a view to liberate the ferric acid. The ferrates of baryta, strontia, and lime are obtained as fine red precipitates when solutions of their salts are mixed with ferrate of potash.

221. *Protosulphate of iron, copperas, green vitriol* or *ferrous sulphate,* is easily obtained by heating 1 part of iron wire with $1\frac{1}{2}$ parts of strong sulphuric acid, mixed with 4 times its weight of water, until the whole of the metal is dissolved, when the solution is allowed to crystallise. Its manufacture on the large scale by the oxidation of iron pyrites has been already referred to.

It forms fine green rhomboidal crystals, having the composition $FeO.SO_3.H_2O.6Aq$.

The colour of the crystals varies somewhat, from the occasional presence of small quantities of the sulphate of sesquioxide of iron ($Fe_2O_3.3SO_3$). It dissolves very easily in twice its weight of cold water, yielding a pale green solution. When the commercial sulphate of iron is boiled with water, it yields a brown muddy solution, in consequence of the decomposition of the sulphate of sesquioxide of iron contained in it, with precipitation of a basic sulphate. The sulphate of iron has a great tendency to absorb oxygen, and to become converted into the sulphate of sesquioxide. Thus, the ordinary crystals when exposed to air gradually become brown, and are converted into a mixture of the neutral and basic sulphates of the sesquioxide of iron—



$$10(FeO.SO_3) + O_5 = 3(Fe_2O_3.3SO_3) + 2Fe_2O_3.SO_3.$$

This disposition to absorb oxygen renders the sulphate of iron useful as a reducing agent; thus, it is employed for precipitating gold in the metallic state from its solutions. But its chief use is for the manufacture of ink and black dyes, by its action upon vegetable infusions containing tannic acid, such as that of nut-galls. This application will be more particularly noticed hereafter.

Sulphate of sesquioxide of iron, or *persulphate of iron,* or *ferric sulphate,* is found in Chili as a white silky crystalline mineral, *coquimbite,* having the composition, $Fe_2O_3.3SO_3.9Aq$.

The *phosphates* of protoxide and sesquioxide of iron are found associated in the mineral known as *vivianite* or *native Prussian blue.*

222. *Sesquichloride,* or *perchloride of iron* or *ferric chloride* (Fe_2Cl_6), is obtained in beautiful dark green crystalline scales when iron wire is heated in a glass tube through which a current of dry chlorine is passed, the sesquichloride passing off in vapour, and condensing in the cool part of the tube. The crystals almost instantly become wet when exposed to air, on account of their great attraction for water. The perchloride of iron may be obtained in solution by dissolving iron in hydrochloric acid, and converting the protochloride of iron ($FeCl_2$) thus formed into perchloride by the action of nitric and hydrochloric acids (p. 172). The solution of perchloride of iron has been recommended in some cases as a disinfectant, being easily reduced to protochloride, and thus affording chlorine to unstable organic matters in contact with it (p. 152). A solution of perchloride of iron in alcohol is used in medicine under the name of *tincture of iron.*

Solution of perchloride of iron is capable of dissolving a very large quantity of *pure* freshly precipitated peroxide of iron, nine molecules of Fe_2O_3 being dissolved by one molecule of Fe_2Cl_6. The solution of *oxychloride of iron* thus obtained has a very dark

red colour, and yields a very copious brown precipitate with common water, or any solution containing even a trace of a sulphate.

223. *Equivalent and atomic weights of iron.*—When iron is dissolved in hydrochloric acid, 28 parts by weight of iron combine with 1 eq. (35·5 parts) of chlorine, displacing 1 part of hydrogen; hence 28 is the equivalent weight of iron.

The specific heat of iron and its isomorphism with magnesium, zinc, and cadmium, show that its atomic weight must be represented by double the equivalent, or 56, so that iron is a diatomic or bivalent element.

The molecular formula of ferric chloride has been confirmed by the determination of the specific gravity of its vapour, which has been found to be 165 times that of hydrogen. If, therefore, one volume (or one atom) of hydrogen be represented as having a weight = 1, *two* volumes (or one molecule) of ferric chloride vapour would weigh (165 × 2) 330, a number nearly agreeing with the sum of two atoms of iron (112) and six atoms of chlorine (213·0).

It will be remarked that iron possesses a different atomicity accordingly as it exists in ferrous or ferric compounds. Thus, in ferrous oxide (FeO) and ferrous chloride ($FeCl_2$), it occupies the place of two atoms of hydrogen, and is diatomic; but in ferric oxide (Fe_2O_3) and ferric chloride (Fe_2Cl_6) each atom of iron occupies the place of three atoms of hydrogen, and is triatomic. Some chemists designate the diatomic iron existing in ferrous compounds by the name *ferrosum* (Fe″), and the triatomic iron of the ferric compounds by *ferricum* (Fe‴).

MANGANESE.

Mn″ = 55 parts by weight.

224. Manganese much resembles iron in several particulars relating both to its physical and chemical characters, and is often found in nature, associated, in small quantities, with the compounds of that metal. The metal itself has not been applied to any useful purpose.

It is obtained by reducing carbonate of manganese ($MnO.CO_2$) with charcoal, at a very high temperature, when a fused mass, composed of manganese combined with a little carbon (corresponding to cast-iron), is obtained, which is freed from carbon by a second fusion in contact with carbonate of manganese.

Metallic manganese is darker in colour than (wrought) iron, and very much harder; it is brittle, and only feebly attracted by the magnet. It is somewhat more easily oxidised than iron.

225. *Oxides of manganese.*—Three distinct compounds of manganese with oxygen have been obtained in the separate state, and two others are believed to exist in combination, but have not been satisfactorily made out in the anhydrous state—

Protoxide of manganese,	MnO
Sesquioxide ,,	Mn_2O_3
Binoxide or peroxide of manganese,	MnO_2
Manganic acid (?)	MnO_3
Permanganic acid (?)	Mn_2O_7.

The *binoxide of manganese* is the chief form in which this metal is found in nature, and is the source from which all other compounds of manganese

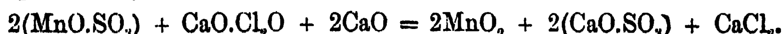
are obtained. Its chief mineral form is *pyrolusite*, which forms steel-grey prismatic crystals; but it is also found amorphous, as *psilomelane*, and in the hydrated state as *wad*. In commerce pyrolusite is known as black manganese, or simply manganese, and is largely imported from Germany, Spain, &c., for the use of the manufacturer of bleaching-powder, the glass-maker, &c. It is also used as a cheap source of oxygen, which it evolves when heated to redness, leaving the *red oxide of manganese*, Mn_3O_4. The binoxide of manganese is an indifferent oxide, and does not combine with acids; when heated with strong sulphuric acid, it loses half its oxygen, and forms the protoxide of manganese, which is a powerful base, and combines with the sulphuric acid to form sulphate of manganese—



$$MnO_2 + H_2O.SO_3 = MnO.SO_3 + H_2O + O.$$

Since the natural binoxide contains peroxide of iron, some persulphate of iron is formed at the same time; but if the mixture be dried and heated to redness, the iron-salt is decomposed, evolving sulphuric acid, and leaving peroxide of iron; while the protoxide of manganese, being a stronger base, does not abandon its sulphuric acid; and the sulphate of manganese may be dissolved out of the mass by treatment with water. On evaporating the solution, and allowing it to cool, it deposits light pink crystals of sulphate of manganese, $MnO.SO_3.H_2O.4Aq$.

This salt is employed by the dyer and calico-printer in the production of black and brown colours. When a solution of sulphate of manganese is mixed with solution of chloride of lime (p. 151), it gives a black precipitate of hydrated peroxide of manganese—



$$2(MnO.SO_3) + CaO.Cl_2O + 2CaO = 2MnO_2 + 2(CaO.SO_3) + CaCl_2.$$

By decomposing a solution of sulphate of manganese with potash or soda, a white precipitate of *hydrated protoxide of manganese* is obtained, which becomes brown when exposed to the air, absorbing oxygen, and becoming converted into the hydrated sesquioxide of manganese.

If solution of sulphate of manganese be mixed with carbonate of soda, a white precipitate of *carbonate of manganese*, $2(MnO.CO_2).H_2O$, is obtained. The pink crystallised mineral *manganese spar* consists of carbonate of manganese ($MnO.CO_2$).

Protoxide of manganese (MnO) itself is obtained as a green powder by heating carbonate of manganese in a tube through which hydrogen is passed to exclude the air, which would convert the protoxide into red oxide (Mn_3O_4). The protoxide has been obtained in transparent emerald-green crystals.

Sesquioxide of manganese, crystallised in octahedra, forms the mineral *braunite*, and, in combination with water, the prismatic crystals of *manganite* ($Mn_2O_3.H_2O$), which often occurs in the commercial ores of manganese. The sesquioxide is a weak base, dissolving in acids to form deep red solutions, which evolve oxygen when heated, leaving salts of the protoxide of manganese. The sulphate of sesquioxide of manganese combines with sulphate of potash to form *manganese-alum* $K_2O.SO_3, Mn_2O_3.3SO_3.24Aq.$, corresponding in crystalline form, as in composition, to alumina-alum. When binoxide of manganese in minute quantity is added to melted glass, it imparts a purple colour, which is probably due to the formation of a silicate of sesquioxide of manganese. The amethyst is believed by some to owe its colour to the same cause.

Red oxide of manganese (Mn_3O_4) is the most stable of the oxides

of this metal, and is formed when either of the others is heated in air. Thus obtained, it has a brown or reddish colour; but it is found in nature as the black mineral *hausmannite*. In composition it resembles the magnetic oxide of iron, but it seems probable that its true formula is $2MnO.MnO_2$, for when treated with diluted nitric acid it leaves the black hydrated binoxide.

When a compound containing manganese, in however small a quantity, is fused on a piece of platinum foil with carbonate of soda (fig. 127), a mass of manganate of soda (Na_2MnO_4) is formed, which is green while hot, and becomes blue on cooling. The oxygen required to convert the lower oxides of manganese into manganic acid has been absorbed from the air.

Manganic acid is obtained in combination with potash, by mixing finely powdered binoxide of manganese into a paste with an equal weight of hydrate of potash dissolved in a little water, drying the paste, and heating it to dull redness in a glass tube, through which oxygen is passed as long as it is absorbed. When the mass is treated with a little cold water, it gives a dark emerald-green solution, and by evaporating this over oil of vitriol, *in vacuo*, dark-green crystals of *manganate of potash* (K_2MnO_4) are formed, which have the same crystalline form as those of sulphate of potash. These crystals dissolve unchanged in water containing potash; but when dissolved in pure water, they yield a red solution of permanganate of potash, and a precipitate of binoxide of manganese—



$$3(K_2O.MnO_3) + 2H_2O = K_2O.Mn_2O_7 + MnO_2 + 2(K_2O.H_2O).$$

The change is more completely effected by adding a little free acid, even carbonic acid. The changes of colour thus produced have acquired for the manganate of potash the name *chameleon mineral*. The solution of manganate of potash (containing free potash) is very easily decomposed by substances having an attraction for oxygen. Thus, most organic substances abstract oxygen from it, and cause the separation of brown sesquioxide of manganese; filtering its solution through paper will even effect this change. The offensive emanations from putrefying organic matters are at once oxidised and rendered inodorous by manganate of potash or soda.

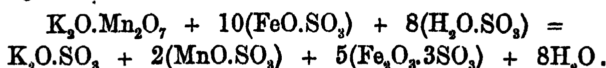
Manganate of soda (Na_2MnO_4) obtained by heating binoxide of manganese with hydrate of soda, under free exposure to air, is employed in a state of solution in water, as *Condy's green disinfectant fluid*. It is also used as a bleaching agent, and in the preparation of oxygen at a cheap rate.

The temporary formation of manganic acid affords a probable explanation of the effect of binoxide of manganese in facilitating the disengagement of oxygen from chlorate of potash (p. 31).

Permanganic acid has been obtained in a hydrated crystalline state by decomposing the permanganate of baryta with sulphuric acid, and evaporating the solution *in vacuo*. It is a brown substance, easily dissolving in water to a red liquid, which is decomposed at about 90° F., evolving oxygen, and depositing binoxide of manganese.

Permanganate of potash, ($K_2O.Mn_2O_7$, or $KMnO_4$), is largely used in many chemical operations. In order to prepare it, 4 parts of finely powdered binoxide of manganese are intimately mixed with 3½ parts of chlorate of potash, and 5 parts of hydrate of potash dissolved in a very little water. The pasty mass is dried, and heated to dull redness for some time in an iron tray or earthen crucible. The oxygen derived from

the chlorate of potash converts the binoxide of manganese into manganic acid, which combines with the potash of the hydrate. On treating the cold mass with water, the manganate of potash is dissolved, forming a dark-green solution. This is diluted with water, and a stream of carbonic acid gas passed through it as long as any change of colour is observed; the carbonic acid combines with the excess of potash, the presence of which conferred stability upon the manganate, which is then decomposed into permanganate of potash and binoxide of manganese. The latter is allowed to settle, and the clear red solution poured off and evaporated to a small bulk. On cooling, it deposits prismatic crystals of the permanganate of potash ($K_2O.Mn_2O_7$), which are red by transmitted light, but reflect a dark-green colour. The carbonate of potash, being much more soluble in water, is left in the solution. Permanganate of potash is remarkable for its great colouring power, a very small quantity of the salt producing an intense purplish-red colour in a large quantity of water. Its solution in water is very easily decomposed by substances having an attraction for oxygen, such as sulphurous acid or a ferrous salt, the permanganic acid being reduced to protoxide of manganese, so that the solution becomes colourless. If a very small piece of iron wire be dissolved in diluted sulphuric acid, the solution of ferrous sulphate so produced will decolorise a large volume of weak solution of the permanganate, being converted into ferric sulphate—



$$K_2O.Mn_2O_7 + 10(FeO.SO_3) + 8(H_2O.SO_3) = K_2O.SO_3 + 2(MnO.SO_3) + 5(Fe_2O_3.3SO_3) + 8H_2O.$$

This decomposition forms the basis of a valuable method for determining the proportion of iron in its ores.

Many organic substances are easily oxidised by permanganate of potash, and this is the case especially with the offensive emanations from putrescent organic matter. Hence it is extensively used, under the name of *Condy's red disinfecting fluid*, in cases where a solid or liquid substance is to be deodorised.

226. *Chlorides of manganese.*—There appear to be three compounds of manganese with chlorine, corresponding to three of the oxides, viz., $MnCl_2$, Mn_2Cl_6 and $MnCl_4$; but only the first is obtainable in the pure state, the others forming solutions, which are easily decomposed with evolution of chlorine.

The *protochloride of manganese* ($MnCl_2$) is obtained in large quantity, as a waste product in the preparation of chlorine, for the manufacture of bleaching-powder. Since there is no useful application for it, the manufacturer sometimes reconverts it into the black oxide. As the native binoxide always contains iron, the liquor obtained by treating it with hydrochloric acid contains sesquichloride of iron (Fe_2Cl_6) mixed with chloride of manganese ($MnCl_2$). In order to separate the iron, advantage is taken of the circumstance that sesquioxides are weaker bases than the protoxides, so that if a small proportion of lime be added to the solution, the iron may be precipitated as sesquioxide, without decomposing the chloride of manganese—



$$Fe_2Cl_6 + 3CaO = Fe_2O_3 + 3CaCl_2.$$

The solution of chloride of manganese is then mixed with chalk, and subjected to the action of steam at a pressure of about two atmospheres. Carbonate of manganese is precipitated ($MnCl_2 + CaO.CO_2 = CaCl_2 + MnO.CO_2$), and when this is dried and heated to about 300° in a current of moist air, the carbonic acid is expelled, and a large proportion of the oxide of manganese is converted into binoxide, which may be employed again for the preparation of chlorine.

According to Weldon's process (page 145), the iron is precipitated as peroxide

by adding chalk, which leaves the manganese in solution; *an excess* of lime is then added and air blown through the mixture at about 150° F., when the white precipitate of MnO, formed at first, absorbs the oxygen, and becomes a black compound of MnO_2 with lime which is used over again for the preparation of chlorine. Unless the lime is added in excess, only $MnO.MnO_2$ is formed, so that the excess of lime displaces the MnO and allows it to be converted into MnO_2. In another process, Weldon employs magnesia instead of lime, with the view of afterwards recovering the chlorine from the chloride of magnesium, in the form of hydrochloric acid (see p. 282), and using the magnesia over again.

By dissolving permanganate of potash in oil of vitriol, and adding fragments of fused chloride of sodium, a remarkable greenish-yellow gas is obtained, which gives purple fumes with moist air, and is decomposed by water, yielding a red solution which contains hydrochloric and permanganic acids. It, therefore, must contain manganese and chlorine, and is sometimes regarded as the perchloride ($MnCl_7$) corresponding to permanganic acid; but it is more probably an oxychloride of manganese (*see* Chlorochromic acid). Care is required in its preparation, which is sometimes attended with explosion.

COBALT.

Co″ = 59 parts by weight.

227. Some of the compounds of cobalt are of considerable importance in the arts, on account of their brilliant and permanent colours. It is generally found in combination with arsenic and sulphur, forming *tin-white cobalt*, $CoAs_2$ and *cobalt glance*, $CoAs_2.CoS_2$, but its ores also generally contain nickel, copper, iron, manganese, and bismuth.

The metal itself is obtained by strongly heating the oxalate of cobalt (CoC_2O_4) in a covered porcelain crucible. In its properties it closely resembles iron, but is said to surpass it in tenacity.

Two *oxides of cobalt* are known—the *protoxide*, CoO, which is decidedly basic, and the *sesquioxide*, Co_2O_3, which is a very feeble base. The protoxide of cobalt, like those of iron and manganese, tends to absorb oxygen from the air, and when heated in air, becomes converted into $CoO.Co_2O_3$, corresponding to the magnetic oxide of iron. The commercial oxide of cobalt, which is employed for painting on porcelain, is obtained by roasting the ore, in order to expel part of the sulphur and arsenic, dissolving it in hydrochloric acid, and precipitating the sesquioxide of iron by the careful addition of lime, when the remaining arsenic is also precipitated as arseniate of iron. Hydrosulphuric acid is passed through the acid solution to precipitate the bismuth and copper, leaving the cobalt and nickel in solution. The latter having been boiled to expel the excess of hydrosulphuric acid, is neutralised with lime and mixed with solution of chloride of lime, which precipitates the sesquioxide of cobalt as a black powder, leaving the oxide of nickel in solution, from which it may be precipitated by the addition of lime.

The salts of oxide of cobalt have a fine red colour in the hydrated state, or in solution, but are generally blue when anhydrous. The silicate of cobalt associated with silicate of potash forms the blue colour known as *smalt*, which is prepared by roasting the cobalt-ore, so as to convert the bulk of the cobalt into oxide, leaving, however, a considerable quantity of arsenic and sulphur still in the ore. The residue is then fused in a crucible with ground quartz and carbonate of potash, when a blue glass is formed, containing silicate of cobalt and silicate of potash, whilst the iron, nickel, and copper, combined with arsenic and sulphur, collect at the bottom of the crucible and form a fused mass of metallic appearance known as *speiss*, which is employed as a source of nickel. The blue glass

is poured into cold water, so that it may be more easily reduced to the fine powder in which the smalt is sold. If the cobalt-ore destined for smalt be over roasted, so as to convert the iron into oxide, this will pass into the smalt as a silicate, injuring its colour.

Zaffre is prepared by roasting a mixture of cobalt-ore with two or three parts of sand.

Thénard's blue consists of phosphate of cobalt and phosphate of alumina, and is prepared by mixing precipitated alumina with phosphate of cobalt and calcining in a covered crucible. The phosphate is obtained by precipitating a solution of nitrate of cobalt with phosphate of potash or soda.

Rinman's green is prepared by calcining the precipitate produced by carbonate of soda in a mixture of sulphate of cobalt with sulphate of zinc. It is a compound of the oxides of cobalt and zinc.

Chloride of cobalt ($CoCl_2$), obtained by dissolving oxide of cobalt in hydrochloric acid, forms red hydrated crystals, which become blue when their water is expelled. If strong hydrochloric acid be added to a red solution of this salt, it becomes blue; if enough water be now added to render it pink, the blue colour may be produced at pleasure by boiling, the solution first passing through a neutral tint. Chloride of cobalt is employed as a *sympathetic ink*, for characters written with its pink solution are nearly invisible till they are held before the fire, when they become blue, and resume their original pink colour if exposed to the air; a little chloride of iron causes a green colour.

The *sulphide of cobalt* (CoS) is obtained as a black precipitate when an alkaline sulphide is added to a solution of a salt of cobalt. A *sesquisulphide* (Co_2S_3) is found in grey octahedra, *cobalt pyrites*. The *bisulphide* (CoS_2) has been obtained artificially.

When ammonia in excess is added to a solution of a salt of cobalt, a deep red liquid is produced, which rapidly absorbs oxygen from the air, especially if hydrochlorate of ammonia be present, giving rise to the production of some remarkable and complex bases which contain the elements of ammonia and of different oxides of cobalt.

NICKEL.

$Ni'' = 59$ parts by weight.

228. Nickel owes its value in the useful arts chiefly to its property of imparting a white colour to the alloys of copper and zinc, with which it forms the alloy known as *German silver*. Nickel is very nearly allied to cobalt, and generally occurs associated with that metal in its ores. One of the principal ores of nickel is the *Kupfernickel* or copper-nickel, so called by the German miners because they frequently mistook it for an ore of copper; it has a reddish metallic appearance, and the formula $NiAs$. *Grey nickel ore* or *nickel glance* is an arseniosulphide of nickel, $NiAs_2.NiS_2$. *Arsenical nickel*, $NiAs_2$ corresponds to tin-white cobalt. The metal is commonly extracted from the *speiss* separated during the preparation of smalt from cobalt-ores (p. 327); the oxide of nickel prepared by the method described above, when strongly heated in contact with charcoal, yields metallic nickel containing carbon.

The pure metal is obtained by igniting the oxalate, as in the case of cobalt, which it much resembles in properties.

The *oxides of nickel* correspond in composition to those of cobalt. The salts formed by the oxide of nickel (NiO) are usually green, and give

bright green solutions. The hydrated oxide has a characteristic apple-green colour, and does not absorb oxygen from the air like the hydrated oxide of cobalt. The greater facility with which the latter is converted into sesquioxide has been applied (as above described) to effect the separation of the two metals. Oxide of nickel has been found native in octahedral crystals, which have also been obtained accidentally in a copper-smelting furnace.

Sulphate of nickel ($NiO.SO_3.H_2O.6Aq.$) forms fine green prismatic crystals, the water of constitution in which may be displaced by sulphate of potash, forming the *double sulphate of nickel and potash*, $NiO.SO_3$, ($K_2O.SO_3.6Aq.$), which crystallises so readily that it was at one time the form in which nickel was separated from the other metals present in its ores.

Three *sulphides of nickel* are known—a *subsulphide*, Ni_2S; a *protosulphide*, NiS, found native as *capillary pyrites*, and obtained as a black precipitate by the action of an alkaline sulphide upon a salt of nickel; and a *bisulphide*, NiS_2.

CHROMIUM.

Cr = 52·5 parts by weight.

229. This metal derives its name from χρῶμα, *colour*, in allusion to the varied colours of its compounds, upon which their uses in the arts chiefly depend. It is comparatively seldom met with, its principal ore being the *chrome-iron ore* ($FeO.Cr_2O_3$), which is remarkable for its resistance to the action of acids and other chemical agents. It is chiefly found in Sweden, Russia, and the United States, and is imported for the manufacture of *bichromate of potash* ($K_2O.2CrO_3$), which is one of the chief commercial compounds of chromium. The ore is first heated to redness and thrown into water, in order that it may be easily ground to a fine powder, which is mixed with carbonate of potash, chalk being added to prevent the fusion of the mass, and strongly heated in a current of air on the hearth of a reverberatory furnace, the mass being occasionally stirred to expose a fresh surface to the air. The oxide of iron is thus converted into sesquioxide, and the sesquioxide of chromium (Cr_2O_3) also absorbs oxygen from the air, becoming *chromic acid* (CrO_3), which combines with the potash to form chromate of potash ($K_2O.CrO_3$). Nitre is sometimes added to hasten the oxidation. On treating the mass with water, a yellow solution of chromate of potash is obtained, which is drawn off from the insoluble residue of sesquioxide of iron and lime, and mixed with a slight excess of nitric acid—



$$\underset{\text{Chromate of potash.}}{2(K_2O.CrO_3)} + H_2O.N_2O_5 = \underset{\text{Bichromate of potash.}}{K_2O.2CrO_3} + K_2O.N_2O_5 + H_2O.$$

The solution, when evaporated, deposits beautiful red tabular crystals of bichromate of potash, which dissolve in 10 parts of cold water, forming an acid solution. It is from this salt that the other compounds of chromium are immediately derived.

Metallic chromium has received no useful application. It has been obtained in octahedral crystals by the action of sodium on sesquichloride of chromium, and in a pulverulent state by the action of potassium. In the latter condition it is easily acted on by acids, but the crystallised chromium is insoluble even in nitro-hydrochloric acid. Like aluminum,

it is more easily attacked by hydrated alkalies at a high temperature, evolving hydrogen and producing chromates. It is remarkably infusible.

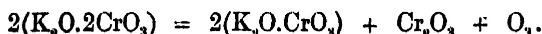
230. Oxides of Chromium.—Two oxides of chromium are known in the separate state—the sesquioxide, Cr_2O_3, and chromic acid, CrO_3. Protoxide of chromium (CrO) is known in the hydrated state, and perchromic acid (Cr_2O_7) is believed to exist in solution.

Chromic acid, the most important of these, is obtained by adding to one measure of a solution of bichromate of potash, saturated at 130° F., one measure and a-half of concentrated sulphuric acid, by small portions at a time, and allowing the solution to cool, when chromic acid crystallises out in fine crimson needles, which are deliquescent, very soluble in water, and decomposed by a moderate heat into oxygen and sesquioxide of chromium. Chromic acid is a powerful oxidising agent; most organic substances, even paper, will reduce it to the green sesquioxide of chromium. A mixture of bichromate of potash and sulphuric acid is employed for bleaching some oils, the colouring matter being oxidised at the expense of the chromic acid, and sulphate of sesquioxide of chromium produced—



$$K_2O.2CrO_3 + 4(H_2O.SO_3) = K_2O.SO_3 + Cr_2O_3.3SO_3 + O_3 + 4H_2O.$$

The bichromate itself evolves oxygen when heated to bright redness, being first fused, and afterwards decomposed—



$$2(K_2O.2CrO_3) = 2(K_2O.CrO_3) + Cr_2O_3 + O_3.$$

Neutral chromate of potash ($K_2O.CrO_3$) is formed by adding carbonate of potash to the red solution of bichromate of potash until its red colour is changed to a fine yellow, when it is evaporated and allowed to crystallise. It forms yellow prismatic crystals having the same form as those of sulphate of potash, and is far more soluble in water than the bichromate, yielding an alkaline solution. It becomes red when heated, and fuses without decomposition.

Terchromate of potash ($K_2O.3CrO_3$) has been obtained in red crystals by adding nitric acid to the bichromate.

Chrome-yellow is the *chromate of lead* ($PbO.CrO_3$), prepared by mixing dilute solutions of acetate of lead and chromate of potash. It is largely used in painting and calico-printing, and by the chemist as a source of oxygen for the analysis of organic substances, since, when heated, it fuses to a brown mass, which evolves oxygen at a red heat. Chrome-yellow being a poisonous salt, its occasional use for colouring confectionery is very objectionable. Chromate of lead in prismatic crystals forms the rather rare *red lead ore of Siberia*, in which chromium was first discovered.

Orange chrome is a *basic chromate of lead* ($2PbO.CrO_3$), and may be obtained by boiling the yellow chromate with lime—



$$2(PbO.CrO_3) + CaO = 2PbO.CrO_3 + CaO.CrO_3.$$

The calico-printer dyes the stuff with yellow chromate of lead, and converts it into orange chromate by a bath of lime-water.

The colour of the *ruby* (crystallised alumina) appears to be due to the presence of a small proportion of chromic acid.

Sesquioxide of chromium (Cr_2O_3) is valuable as a green colour, especially for glass and porcelain, since it is not decomposed by heat. It is prepared by heating bichromate of potash with one-fourth of its weight of starch, the carbon of which deprives the chromic acid of half its oxygen, leaving

a mixture of sesquioxide of chromium with carbonate of potash, which may be removed by washing with water. If sulphur be substituted for the starch, sulphate of potash will be formed, which may also be removed by water. When the sesquioxide of chromium is strongly heated, it exhibits a sudden glow, becomes darker in colour, and insoluble in acids which previously dissolved it easily; in this respect it resembles alumina and sesquioxide of iron. Like these oxides, the sesquioxide of chromium is a feeble base; it is remarkable for forming two classes of salts containing the same proportions of acid and base, but differing in the colour of their solutions, and in some other properties. Thus, there are two modifications of the *sulphate of sesquioxide of chromium*—the green sulphate, $Cr_2O_3.3SO_3.5Aq.$, and the violet sulphate, $Cr_2O_3.3SO_3.15Aq.$ The solution of the latter becomes green when boiled, being converted into the former. *Chrome-alum* forms dark purple octahedra ($K_2O.SO_3,Cr_2O_3.3SO_3.24Aq.$) which contain the violet modification of the sulphate; and if its solution in water be boiled, its purple colour changes to green, and the solution refuses to crystallise.* The anhydrous sulphate of chromium forms red crystals, which are insoluble in water and acids. A green basic *borate of sesquioxide of chromium* is used in painting and calico-printing, under the name of *vert de Guignet*, and is prepared by strongly heating bichromate of potash with 3 parts of crystallised boracic acid, when borate of potash and borate of chromium are formed, half the oxygen of the chromic acid being expelled. The borate of potash and the excess of boracic acid are afterwards washed out by water. By reducing an alkaline chromate with hyposulphite of soda, the compound $Cr_2O_3.CrO_3$ has been obtained as a brown precipitate.

Protoxide of chromium (CrO) is not known in the pure state, but is precipitated as a brown hydrate when protochloride of chromium is decomposed by potash. It absorbs oxygen even more readily than protoxide of iron, becoming converted into a hydrated proto-sesquioxide of chromium ($CrO.Cr_2O_3$), corresponding in composition to the magnetic oxide of iron. The protoxide of chromium is a feeble base; a double sulphate of protoxide of chromium and potash ($CrO.SO_3,K_2O.SO_3.6Aq.$) is known, which has the same crystalline form as the corresponding iron salt ($FeO.SO_3,K_2O.SO_3.6Aq.$); it has a blue colour, and gives a blue solution, which becomes green when exposed to air, from the formation of sesquioxide of chromium.

Perchromic acid ($HCrO_4$, or $H_2O.Cr_2O_7$), is believed to exist in the blue solution obtained by the action of peroxide of hydrogen upon solution of chromic acid, but neither the acid nor its salts have been obtained in a separate state.

231. *Chlorides of chromium.*—The *sesquichloride of chromium* (Cr_2Cl_6), obtained by passing dry chlorine over a mixture of sesquioxide of chromium with charcoal, heated to redness in a glass tube, is converted into vapour, and condenses upon the cooler part of the tube in shining leaflets, having a fine violet colour. Cold water does not affect them, but boiling water slowly dissolves them to a green solution resembling that obtained by dissolving sesquioxide of chromium in hydrochloric acid.

Protochloride of chromium ($CrCl_2$) results from the action of hydrogen, at a red heat, upon the sesquichloride. Strange to say, it is white, and dissolves in water to form a blue solution which absorbs oxygen from the air, becoming green. It is remarkable that if the violet sesquichloride of chromium is suspended in water, and a minute quantity of the protochloride added, the sesquichloride immediately dissolves to a green solution, evolving heat.

Chlorochromic acid (CrO_2Cl_2) is a very remarkable brown-red liquid, obtained by

* Exposure to cold, it is said, again converts it into the crystallisable violet form.

distilling 10 parts of common salt and 17 of bichromate of potash, previously fused together and broken into fragments, with 40 parts of oil of vitriol—



$$K_2O.2CrO_3 + 4NaCl + 3(H_2O.SO_3) = K_2O.SO_3 + 2(Na_2O.SO_3) + 3H_2O + 2CrO_2Cl_2.$$

It much resembles bromine in appearance, and fumes very strongly in air, the moisture of which decomposes its red vapour, forming chromic and hydrochloric acids; $CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$. It is a very powerful oxidising and chlorinating agent, and inflames ammonia and alcohol when brought in contact with them.

It is occasionally used to illustrate the nature of illuminating flames; for if hydrogen be passed through a bottle containing a few drops of chlorochromic acid, the gas becomes charged with its vapour, and, if kindled, burns with a brilliant white flame, which deposits a beautiful green film of sesquioxide of chromium upon a cold surface.

The name *oxychloride of chromium*, applied to this compound, is more correct than chlorochromic acid, for it is not known to form salts. When chlorochromic acid is heated, in a sealed tube, to 370° F., it is converted into a black solid body, according to the equation $3CrO_2Cl_2 = Cl_4 + CrCl_2.2CrO_3$.*

Fluoride of chromium (CrF_6) is another volatile compound of chromium, obtained by distilling chromate of lead with fluor spar and sulphuric acid; it is a red gas, condensible to a red liquid at a low temperature. Water decomposes it, yielding chromic and hydrofluoric acids.

Sesquisulphide of chromium (Cr_2S_3) is formed when vapour of bisulphide of carbon is passed over sesquioxide of chromium heated to redness. It forms black lustrous scales resembling graphite.

232. *General review of zinc, iron, cobalt, nickel, manganese, and chromium.*—Many points of resemblance will have been noticed in the chemical history of these metals to justify their being classed in the same group. They are all capable of decomposing water at a red heat, and easily displace hydrogen from hydrochloric acid. Each of them forms a base by combining with one atom of oxygen, and these oxides produce salts which have the same crystalline form. All these oxides, except those of zinc and nickel, easily absorb oxygen from the air, and are converted into sesquioxides. Zinc does not form a sesquioxide, and the sesquioxide of nickel is an indifferent oxide, while that of cobalt is very feebly basic; the sesquioxide of manganese is a stronger base, and the basic properties of the sesquioxides of chromium and iron are very decided. Zinc and nickel do not exhibit any tendency to form a well-marked acid oxide, but the existence of an acid oxide of cobalt is suspected; and iron, manganese, and chromium form undoubted acids with three equivalents of oxygen. Zinc and nickel are only known to form one compound with chlorine; cobalt and manganese form, in addition to their protochlorides, very unstable sesquichlorides known only in solution, but iron and chromium form very stable volatile sesquichlorides. The metals composing this group are all bivalent or diatomic,* and are found associated in natural minerals; this is especially the case with iron, manganese, cobalt, and nickel. They are all attracted by the magnet, with the exception of zinc, and, with the same exception, require a very high temperature for their fusion. Through zinc, the metals of this group are connected with magnesium, which resembles it in volatility, in combustibility, and in the crystalline form of its salts. Iron and chromium connect this group with aluminum, their sesquioxides being isomorphous with alumina, and their sesquichlorides volatile like that of aluminum.

* Chromium, like iron, is triatomic in the sesquioxides and the compounds derived from it, and, in chromic acid, it must be regarded as hexatomic.

COPPER.

$Cu'' = 63\cdot5$ parts by weight.

233. Metallic copper is met with in nature more abundantly than *metallic* iron, though the compounds of the latter metal are of more frequent occurrence than those of the former.* A very important vein of metallic copper, of excellent quality, occurs near Lake Superior in North America, from which 6000 tons were extracted in 1858. Metallic copper is also sometimes found in Cornwall; and *copper sand*, containing metallic copper and quartz, is imported from Chili.

234. *Ores of copper.*—The most important English ore of copper is *copper pyrites*, which is a double sulphide, containing copper, iron, and sulphur in the proportions indicated by the formula $CuFeS_2$. It may be known by its beautiful brass yellow colour and metallic lustre. Copper pyrites is found in Cornwall and Devonshire, and is generally associated with arsenical pyrites ($FeS_2.FeAs_2$), tinstone (SnO_2), quartz, fluor spar, and clay. A very attractive variety of copper pyrites is called *variegated copper ore* or *peacock copper*, in allusion to its rainbow colours; its simplest formula is Cu_3FeS_3. This variety is found in Cornwall and Killarney.

Copper glance (Cu_2S) is another Cornish ore of copper, of a dark grey colour and feeble metallic lustre.

Grey copper ore, also abundant in Cornwall, is essentially a compound of the sulphides of copper and iron with those of antimony and arsenic, but it often contains silver, lead, zinc, and sometimes mercury.

Malachite, a basic carbonate of copper, is imported from Australia (Burra Burra), and is also found abundantly in Siberia. Green malachite, the most beautifully veined ornamental variety, has the composition $CuO.CO_2.CuO.H_2O$, and blue malachite is $2(CuO.CO_2).CuO.H_2O$.

Red copper ore (Cu_2O) is found in West Cornwall, and the black oxide (CuO) is abundant in the north of Chili.

235. The seat of English copper-smelting is at Swansea, which is situated in convenient proximity to the anthracite coal employed in the furnaces. The chemical process by which copper is extracted from the ore includes three distinct operations:—(1), The *roasting*, to expel the arsenic and part of the sulphur, and to convert the sulphide of iron into oxide of iron; (2), the *fusion with silica*, to remove the oxide of iron as silicate, and to obtain the copper in combination with sulphur only; and (3), the *roasting* of this combination of copper with sulphur, in order to expel the latter and obtain metallic copper.

The details of the smelting process appear somewhat complicated, because it is divided into several stages to allow of the introduction of the different varieties of ore to be treated. Thus, the first roasting process is unnecessary for the oxides and carbonates of copper, and the fusion with silica is not needed for those ores which are free from iron, so that they may be introduced at a later stage in the operations.

(1.) *Calcining or roasting the ore, to expel arsenic and part of the*

* Copper is not at all frequently found in animals or vegetables; but Church has made the remarkable observation that the red colouring matter (*turacine*) of the feathers of the plantain-eater (*touraco*) contains as much as 5·9 per cent. of copper.

sulphur.—The ores having been sorted, and broken into small pieces, are mixed so as to contain from 8 to 10 per cent. of copper, and roasted, in

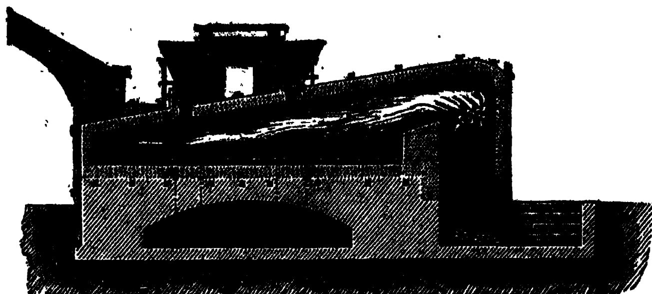


Fig. 255.

quantities of about three tons, for at least twelve hours, on the spacious hearth (H, fig. 256) of a reverberatory furnace (fig. 255), at a temperature insufficient for fusion, being occasionally stirred to expose them freely to the action of the air, which is admitted into the furnace through an opening (O) in the side of the hearth upon which the ore is spread. The oxygen of the air converts a part of the sulphur into sulphurous acid gas, and the bulk of the arsenic into arsenious acid, which passes off in the form of vapour. A part of the sulphide of iron is converted into sulphate of iron by absorbing oxygen at an early stage of the process, and this sulphate is afterwards decomposed at a higher temperature, evolving sulphurous and sulphuric acids, and leaving oxide of iron (see p. 322). A portion of the sulphide of copper is also converted into oxide of copper during the roasting, so that the roasted ore consists essentially of a mixture of oxide and sulphide of copper with oxide and sulphide of iron. Since the sulphide of iron is more easily oxidised than sulphide of copper, the greater part of the latter remains unaltered in the roasted ore.

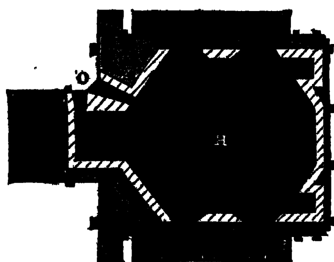


Fig. 256.

During the roasting of copper ore, dense white fumes escape from the furnaces. This *copper-smoke*, as it is termed, contains arsenious, sulphurous, sulphuric, and hydrofluoric acids, the latter being derived from the fluor spar associated with the ore; if allowed to escape, these fumes seriously contaminate the air in the neighbourhood, and copper-smelters are endeavouring to apply some method of condensing, and perhaps turning them to profitable account.

(2.) *Fusion for coarse metal, to remove the oxide of iron by dissolving it with silicic acid at a high temperature.*—The roasted ore is now mixed with *metal slag* from process 4, and with ores containing silicic acid and oxides of copper, but no sulphur; the mixture is introduced into the *ore-furnace* (fig. 257), and fused for five hours at a higher temperature than that employed in the previous operation. In this process fluor spar is sometimes added in order to increase the fluidity of the slag.

The oxide of copper acts upon the sulphide of iron still contained in the roasted ore, with formation of sulphide of copper and oxide of iron; but since there is more sulphide of iron present than the oxide of copper can decompose, the excess of sulphide of iron combines with the sulphide of copper to form a fusible compound, which separates from the slag, and collects in the form of a *matt* or *regulus* of *coarse metal*, in a cavity (C) on the hearth of the furnace; it is run out into a tank of water (T) in order to granulate it, so that it may be better fitted to undergo the next operation.

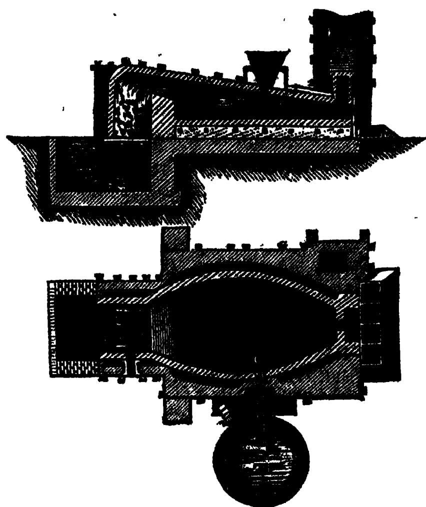


Fig. 257.

The oxide of iron combines with the silicic acid contained in the charge, to form a fusible silicate of iron (*ore-furnace slag*), which is raked out into moulds of sand, and cast into blocks used for rough building purposes in the neighbourhood.

The composition of the coarse metal corresponds pretty closely with the formula $CuFeS_2$. It contains from 33 to 35 per cent. of copper; whilst the original ore, before roasting, is usually sorted so that it may contain about 8·5 per cent.

The ore-furnace *slag* is approximately represented by the formula $FeO.SiO_2$; but it contains a minute proportion of copper, as is shown by the green efflorescence on the walls in which it is used around Swansea. Fragments of quartz are seen disseminated through this slag.

(3.) *Calcination of the coarse metal, to convert the greater part of the sulphide of iron into oxide.*—The granulated coarse metal is roasted at a moderate heat for twenty-four hours, as in the first operation, so that the oxygen of the air may decompose the sulphide of iron, removing the sulphur as sulphurous acid gas, and leaving the iron in the form of oxide.

(4.) *Fusion for white metal, to remove the whole of the iron as silicate.*—The roasted coarse metal is mixed with *roaster* and *refinery* slags from processes 5 and 6, and with ores containing carbonates and oxides of copper, and fused for six hours, as in the second operation. Any sulphide of iron which was left unchanged in the roasting, is now converted into oxide of iron by the oxide of copper, the latter metal taking the sulphur. The whole of the oxide of iron combines with the silicic acid to form a fusible slag, the composition of which is approximately represented by the formula $3FeO.2SiO_2$.

The *matt* or *regulus* of *white metal* which collects beneath the slag is nearly pure subsulphide of copper (Cu_2S), half the sulphur existing in the protosulphide (CuS) having been removed by oxidation in the furnace. The white metal is run into sand-moulds and cast into ingots. The tin and other foreign metals usually collect in the lower part of the ingot, so that, for making *best selected copper*, the upper part is broken off and worked

separately, the inferior copper obtained from the lower part of the ingot being termed *tile-copper*. The ingots of white metal often contain beautiful tufts of metallic copper in the form of *copper moss*.

The slag separated from the white metal (*metal-slag*) is much more fluid than the ore-furnace slag, and contains so much silicate of copper that it is preserved for use in the melting for coarse metal.

(5.) *Roasting the white metal, to remove the sulphur and obtain blistered copper.*—The ingots of white metal (to the amount of about 3 tons) are placed upon the hearth of a reverberatory furnace, and heated for four hours to a temperature just below fusion, so that they may be oxidised at the surface, the sulphur passing off as sulphurous acid, and the copper being converted into oxide. During this roasting the greater part of the arsenic, generally present in the fine metal, is expelled as arsenious acid. The temperature is then raised, so that the charge may be completely fused, after which it is lowered again till the 12th hour. The oxide of copper now acts upon the sulphide of copper to form metallic copper and sulphurous acid gas, which escapes with violent ebullition from the melted mass; $Cu_2S + 2CuO = SO_2 + Cu_4$. When this ebullition ceases, the temperature is again raised so as to cause the complete separation of the copper from the slag, and the metal is run out into moulds of sand. Its name of *blister copper* is derived from the appearance caused by the escape of the last portions of sulphurous acid from the metal when solidifying in the mould.

The slag (*roaster slag*) is formed in this operation by the combination of a part of the oxide of copper with silicic acid derived from the sand adhering to the ingots, and from the hearth of the furnace. The slag also contains the silicates of iron and of other metals, such as tin and lead, which might have been contained in the white metal. This slag is used again in the melting for white metal.

(6.) *Refining, to remove foreign metals.*—This process consists in slowly fusing 7 or 8 tons of the blistered copper in a reverberatory furnace, so that the air passing through the furnace may remove any remaining sulphur as sulphurous acid, and may oxidise the small quantities of iron, tin, lead, &c., present in the metal. Of course, a large proportion of the copper is oxidised at the same time, and the suboxide of copper, together with the oxides of the foreign metals, combine with silicic acid (from the hearth or from adhering sand) to form a slag which collects upon the surface of the melted copper. A portion of the suboxide of copper is dissolved by the metallic copper, rendering it brittle or *dry copper*.

(7.) *Toughening or poling, to remove a part of the oxygen and bring the copper to tough-pitch.*—After about twenty hours, the slag is skimmed from the metal, a quantity of anthracite is thrown over the surface to prevent further oxidation, and the metal is *poled*, *i.e.*, stirred with a pole of young wood, until a small sample, removed for examination, presents a peculiar silky fracture, indicating it to be at *tough-pitch*, when it is cast into ingots.

The chemical change during the poling appears to consist in the removal of the oxygen contained in the suboxide present in the metal, by the reducing action of the combustible gases disengaged from the wood. The presence of a small proportion of suboxide of copper is said to confer greater toughness upon the metal, so that if the poling be continued until

the whole of the oxygen is removed, *overpoled copper* of lower tenacity is obtained. On the other hand, the brittleness of *underpoled copper* is due to the presence of suboxide of copper in too large proportion. *Tough-cake copper* is that which has been poled to the proper extent.

When the copper is intended for rolling, a small quantity (not exceeding ½ per cent.) of lead is generally added to it before it is ladled into the ingot moulds.

The chemical changes which take place during the above processes will be more clearly understood after inspecting the subjoined table, which exhibits the composition of the products obtained at different stages of the process, these being distinguished by the same numerals as were employed in the above description.

Products obtained in smelting Ores of Copper.

In 100 parts.	Ore.	Roasted Ore.	Coarse Metal.	Roasted Coarse Metal.	White Metal.	Blister Copper.	Refined Copper.	Tough-pitch Copper.
		(1.)	(2.)	(3.)	(4.)	(5.)	(6.)	(7.)
Copper, ...	8·2	8·6	33·7	33·7	77·4	98·0	99·4	99·6
Iron, ...	17·9	17·6	33·6	33·6	0·7	0·5	trace	trace
Sulphur, ...	19·9	12·5	29·2	13·0	21·0	0·2	trace	trace
Oxygen, ...	1·0	4·5	...	11·0	...	...	0·4	0·03
Silicic acid, . . .	34·3	34·3						
Sulphuric acid, .	...	1·1						
			Ore Furnace Slag.		Metal Slag.	Roaster Slag.	Refinery Slag.	
			(2.)		(4.)	(5.)	(6.)	
Oxide of iron (FeO), ...			28·5	..	56·0	28·0	3·1	
Suboxide of copper (Cu_2O), . .			0·5	...	0·9	16·9	36·2	
Silicic acid, ...			30·0	...	33·8	47·5	47·4	

Blue metal is the term applied to the regulus of white metal (from process 4), when it still contains a considerable proportion of sulphide of iron, in consequence of a deficient supply of oxide of copper in the furnace. *Pimple metal* is obtained in the same operation when the oxide of copper is in excess, so that a portion of the copper is reduced, as in process 5, with evolution of sulphurous acid, which produces the pimply appearance in escaping. The reduced copper gives a reddish colour to the pimple copper. *Coarse copper* is a similar intermediate stage between white metal and blistered copper. *Tile copper* is that extracted from the bottoms of the ingots of white metal, when the tops have been detached for making best select copper. *Rosette* or *rose copper* is obtained by running water upon the toughened metal, so as to enable the metal to be removed in films. *Anglesea* or *Mona copper* is a very tough copper, reduced by metallic iron from the *blue water* of the copper mines, which contains sulphate of copper.

236. For the purpose of illustration, copper may be extracted from copper pyrites on the small scale in the following manner:—

200 grains of the powdered ore are mixed with an equal weight of dried borax, and fused in a covered earthen crucible (of about 8 oz. capacity), at a full red heat, for about half an hour. The earthy matters associated with the ore are dissolved by the borax, and the pure copper pyrites collects at the bottom of the crucible. The contents of the latter are poured into an iron mould (scorifying mould, fig. 258), and when the mass has set, it is dipped into water. The semi-metallic button is then easily detached from the slag by a gentle blow; it is weighed, finely powdered in an iron mortar, and introduced into an earthen crucible, which is placed obliquely over a dull fire, so that it may not become hot enough to fuse the ore, which should be stirred occasionally with an iron rod to promote the oxidation of the sulphur by the air. When the odour of sulphurous acid is no longer perceptible, the crucible is

placed in a Sefström's blast-furnace (fig. 254), and exposed for a few minutes to a white heat, in order to decompose the sulphates of iron and copper. When no more fumes of sulphuric acid are perceived, the crucible is lifted from the fire, held over the iron mortar, and the roasted ore quickly scraped out of it with a steel spatula. This mixture of the oxides of copper and iron is reduced to a fine powder, mixed with 600 grains of dried carbonate of soda and 60 grains of powdered charcoal, returned to the same crucible, covered with 200 grains of dried borax, and heated in a Sefström's furnace for twenty minutes. The crucible is then allowed to cool partly, plunged into water to render it brittle, and carefully broken to extract the button of metallic copper, which is weighed to ascertain the amount contained in the original ore.

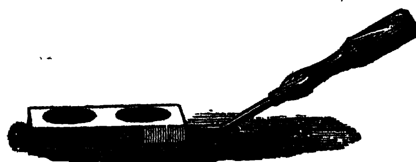


Fig. 258.

237. *Effect of impurities upon the quality of copper.*—The information possessed by chemists upon this subject is still very limited. It has been already mentioned that the presence of a small proportion of *suboxide of copper* in commercial copper is found to increase its toughness. It is believed that copper, perfectly free from metallic impurities, is not improved in quality by the presence of the suboxide, but that this substance has the effect of counteracting the red-shortness (see p. 313) of commercial copper, caused by the presence of foreign metals.

Sulphur, even in minute proportion, appears seriously to injure the malleability of copper.

Arsenic is almost invariably present in copper, very frequently amounting to 0·1 per cent., and does not appear to exercise any injurious influence in this proportion; indeed, its presence is sometimes stated to increase the malleability and tenacity of the metal.

Phosphorus is not usually found in the copper of commerce. When purposely added in quantity varying from 0·12 to 0·5 per cent. it is found to increase the hardness and tenacity of the copper, though rendering it somewhat red-short.

Tin, in minute proportion, is also said to increase the toughness of copper, though any considerable proportion renders it brittle.

Antimony is a very objectionable impurity, and is by no means uncommon in samples of copper.

Nickel is believed to injure the quality of copper in which it occurs.

Bismuth and *silver* are very generally found in marketable copper, but their effect upon its quality has not been clearly determined.

All impurities appear to affect the malleability and tenacity of copper more perceptibly at high than at low temperatures.

The conducting power of copper for electricity is affected in an extraordinary degree by the presence of impurities. Thus, if the conducting power of chemically pure copper be represented by 100, that of the very pure native copper from Lake Superior has been found to be 93, that of the copper extracted from the malachite of the Burra Burra mines in South Australia was 89, whilst that of Spanish copper, remarkable for containing much arsenic, was only 14.

Pure copper is obtained by decomposing a solution of pure sulphate of copper by the galvanic current, as in the *electrotype* process. If the negative wire be attached to a copper plate immersed in the solution, the pure copper may be stripped off this plate in a sheet.

238. *Properties of copper.*—The most prominent character which confers upon copper so high a rank among the useful metals is its malleability, which allows it to be readily fashioned under the hammer, and to be beaten or rolled out into thin sheets; among the metals in ordinary use, only gold and silver exceed copper in malleability, and the comparative scarcity of those metals leads to the application of copper for most purposes where great malleability is requisite.

Although, in tenacity or strength, copper ranks next to iron, it is still very far inferior to it, for a copper wire of $\frac{1}{10}$ inch in diameter will support only 385 lbs., while a similar iron wire will carry 705 lbs. without breaking; and in consequence of its inferior tenacity, copper is less ductile than iron, and does not admit of being so readily drawn into exceedingly thin wires.

The comparative ease with which copper may be fused, allows it to be cast much more readily than iron; for it will be remembered that the latter metal can be liquefied only by the highest attainable furnace heat, whereas copper can be fused at about 2000° F., a temperature generally spoken of as a bright red heat.

As being the most sonorous of metals, copper has been, from time immemorial, employed in the construction of bells and musical instruments. The readiness with which it transmits electricity is turned to account in telegraphic communication, its conducting power being almost equal to that of silver, which is the best of electric conductors. In conducting power for heat, copper is surpassed only by silver and gold.

Copper is not so hard as iron, and is somewhat heavier, the specific gravity of cast copper being 8·92, and that of hammered or drawn copper 8·95.

The resistance of copper to the chemical action of moist air gives it a great advantage over iron for many uses, and the circumstance that it does not decompose water in presence of acids, enables it to be employed as the negative plate in galvanic couples.

239. *Effect of sea-water upon coppe*[illegible] is placed in a solution of salt in water, no perceptib[illegible] but in the course of time, if the air be allowed access, i[illegible] green coating of *oxychloride of copper* ($CuCl_2.3CuO.4H_2$[illegible] consisting, first, in the conversion of the copper into [illegible] and afterwards in the decomposition of the oxide by th[illegible] sodium; $4CuO + 2NaCl = CuCl_2.3CuO + Na_2O$. The surface [illegible] copper is thus corroded, and in the case of a copper-bottomed ship, [illegible] action of sea-water not only occasions a great waste of copper, but roughens the surface of the sheathing, and affords points of attachment to barnacles, &c., which injure the speed of the vessel. Many attempts have been made to obviate this inconvenience. Zinc has been fastened here and there to the outside of the copper, placing the latter in an electronegative condition; the copper has been coated with various compositions, but with very indifferent success. *Muntz metal* or *yellow sheathing*, or *malleable brass*, an alloy of 3 parts of copper and 2 parts of zinc, has been employed with some advantage in place of copper, for it is very much cheaper and somewhat less easily corroded; but the difficulty is by no means overcome. Copper containing about 0·5 per cent. of phosphorus is said to be corroded by sea-water much less easily than pure copper.

240. *Danger attending the use of copper vessels in cooking food.*—The

use of copper for culinary vessels has occasionally led to serious consequences, from the poisonous nature of its compounds, and from ignorance of the conditions under which these compounds are formed. A perfectly clean surface of metallic copper is not affected by any of the substances employed in the preparation of food, but if the metal has been allowed to remain exposed to the action of the air, it becomes covered with a film of oxide of copper, and this subsequently combines with water and carbonic acid derived from the air, to produce a basic carbonate of copper,* which, becoming dissolved, or mixed with the food prepared in these vessels, confers upon it a poisonous character. This danger may be avoided by the use of vessels which are perfectly clean and bright, but even from these, certain articles of food may become contaminated with copper, for this metal is much more likely to be oxidised by the air when in contact with acids (vinegar, juices of fruits, &c.), or with fatty matters, or even with common salt, and if oxide of copper be once formed, it will be readily dissolved by such substances. Hence it is usual to coat the interior of copper vessels with tin, which is able to resist the action of the air, even in the presence of acids and saline matters.

241. *Useful alloys of copper with other metals.*—The most important alloys of which copper is a predominant constituent are included in the following table :—

Composition of 100 parts.

	Copper.	Zinc.	Tin.	Iron.	Nickel.	Aluminum.
Brass, ...	64	36				
Muntz metal, ...	60 to 70	40 to 30				
German silver, . . .	51	30·5	...	...	18·5	
Aich (or Gedge's) metal,	60	38·2	...	1·8		
Sterro-metal, ...	55	42·4	0·8	1·8		
Bell metal, ...	78	...	22			
Speculum metal, . .	66·6	...	33·4			
Bronze, ...	[illegible]	4	16			
Gun metal,	[illegible]	...	9·5			
Bron[illegible]	[illegible]	[illegible]	4			
[illegible]	[illegible]	...	...	...	...	10

[illegible] by melting copper in a crucible, and adding rather more [illegible] its weight of zinc. It is difficult to decide whether brass is a true chemical compound, or a mere mechanical mixture of copper and zinc, because it is capable of dissolving either of those metals when in a state of fusion. The circumstance that it can be deposited by decomposing a solution containing copper and zinc by the galvanic current, would appear to indicate that it is a chemical compound, and its physical properties are not such as would be expected from a mere mixture of its constituents. A small quantity of tin is added to brass intended for door-plates, which renders the engraving much easier. When it has to be turned or filed, about 2 per cent. of lead is usually added to it, in order to prevent it from adhering to the tools employed. Brass cannot be melted without losing a portion of its zinc in the form of vapour. When exposed to frequent vibration (as in the suspending chains of chandeliers) it suffers an alteration in structure and becomes extremely brittle.

* Often [illegible] called *verdigris*, which is really a basic acetate of copper.

The solder used by braziers consists of equal weights of copper and zinc. In order to prevent ornamental brass-work from being tarnished by the action of air, it is either lacquered or bronzed. *Lacquering* consists simply in varnishing the brass with a solution of shell-lac in spirit, coloured with dragon's blood. *Bronzing* is effected by applying a solution of arsenic or mercury, or platinum, to the surface of the brass. By the action of arsenious acid dissolved in hydrochloric acid, upon brass, the latter acquires a coating composed of arsenic and copper, which imparts a bronzed appearance, the zinc being dissolved in place of the arsenic, which combines with the copper at the surface—



$$As_2O_3 + 6HCl + Zn_3 = As_2 + 3ZnCl_2 + 3H_2O .$$

A mixture of corrosive sublimate (bichloride of mercury, $HgCl_2$) and acetic acid is also sometimes employed, when the mercury is displaced by the zinc, and precipitated upon the surface of the brass, with which it forms a bronze-like amalgam. For bronzing brass instruments, such as theodolites, levels, &c., a solution of bichloride of platinum is employed, the zinc of the brass precipitating a very durable film of metallic platinum upon its surface ($PtCl_4 + Zn_2 = Pt + 2ZnCl_2$). *Aich-metal* is a kind of brass containing iron, and has been employed for cannon, on account of its great strength. At a red heat it is very malleable.

Sterro-metal (στερρος, strong) is another variety of brass containing iron and tin, said to have been discovered accidentally in making brass with the alloy of zinc and iron obtained during the process of making galvanised iron (p. 292). It possesses great strength and elasticity, and is used by engineers for the pumps of hydraulic presses.

Aluminum-bronze has been already noticed, and the alloys of copper and tin will be described under the latter metal.

A very hard white alloy of 77 parts of zinc, 17 of tin, and 6 of copper, is sometimes employed for the bearings of the driving-wheels of locomotives.

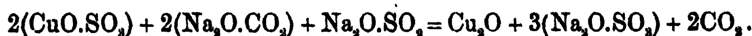
Iron and steel are coated with a [illegible] film of copper, by placing them in contact with metalli[illegible] solution of oxide of copper, prepared by mixing sulpha[illegible] copper [illegible]rate of potash and soda, and caustic soda. The copper [illegible] upon the iron by slow voltaic action, the zinc being [illegible]. By adding a solution of stannate of soda to the alkal[illegible] deposit of bronze may be obtained.

242. Oxides of copper.—Two oxides of copper are well known [illegible] separate state, viz., the suboxide Cu_2O, and the oxide CuO. Another oxide, Cu_4O, has been obtained in a hydrated state, and there is some evidence of the existence of an acid oxide.

The black oxide of copper (cupric oxide), CuO, is the black layer which is formed upon the surface of the metal when heated in air. It is employed by the chemist in the ultimate analysis of organic substances by combustion (p. 80), being prepared for this purpose by acting upon copper with nitric acid to convert it into nitrate of copper (p. 133), and heating this to dull redness in a rough vessel made of sheet copper, when it leaves the black oxide; $CuO.N_2O_5 = 2NO_2 + O + CuO$. At a higher temperature the oxide fuses into a very hard mass; but it cannot be decomposed by heat. Oxide of copper absorbs water easily from the air, but it is not dissolved by water; acids, however, dissolve it, forming the

salts of copper, whence the use of oil of vitriol and nitric acid for cleansing the tarnished surface of copper; a blackened coin, for example, immersed in strong nitric acid, and thoroughly washed, becomes as bright as when freshly coined. Silicic acid dissolves oxide of copper at a high temperature, forming silicate of copper, which is taken advantage of in producing a fine green colour in glass.

Red oxide or *suboxide of copper* (*cuprous oxide*), Cu_2O, is formed when a mixture of 5 parts of the black oxide with 4 parts of copper filings is heated in a closed crucible. It may also be prepared by boiling a solution of sulphate of copper with a solution containing sulphite of soda and carbonate of soda in equal quantities, when the suboxide of copper is precipitated as a reddish yellow powder, which should be washed, by decantation, with boiled water—



$$2(CuO.SO_3) + 2(Na_2O.CO_2) + Na_2O.SO_2 = Cu_2O + 3(Na_2O.SO_3) + 2CO_2.$$

The suboxide of copper is a feeble base, but its salts are not easily obtained by direct union with acids, for these generally decompose it into metallic copper and oxide of copper, which combines with the acid. In the moist state it is slowly oxidised by the air. Ammonia dissolves the suboxide, forming a solution which is perfectly colourless until it is allowed to come into contact with air, when it assumes a fine blue colour, becoming converted into an ammoniacal solution of the oxide. If the blue solution be placed in a stoppered bottle (quite filled with it) with a strip of clean copper, it will gradually become colourless, the oxide being again reduced to suboxide, a portion of the copper being dissolved. When copper filings are shaken with ammonia in a bottle of air, the same blue solution is obtained, the oxidation of the copper being attended with a simultaneous oxidation of a portion of the ammonia, and its conversion into nitrous acid, so that white fumes of nitrite of ammonia are formed in the upper part of the bottle. If the blue solution be poured into a large quantity of water, a light blue precipitate of hydrated oxide of copper is obtained. The ammoniacal solution of oxide of copper has the unusual property of dissolving [illegible] cotton, tow, and other varieties of *cellulose*, this substance being [illegible]ated from the solution on adding an acid.

S[illegible] copper, added [illegible] glass, imparts to it a fine red colour, [illegible] by the glass-maker.

Quadrant[illegible] copper, Cu_4O, has been obtained in combination with [illegible] by the action of protochloride of tin and potash upon a salt of copper.

Cupric acid is believed to be formed when metallic copper is fused with nitre and caustic potash. The mass yields a blue solution in water, which is very easily decomposed, with evolution of oxygen and precipitation of oxide of copper. The existence of an unstable oxide of copper, containing more than one atom of oxygen, is also rendered probable by the circumstance, that oxide of copper acts like binoxide of manganese in facilitating the disengagement of oxygen from chlorate of potash by heat (page 31).

243. *Sulphate of copper.*—The beautiful prismatic crystals known as *blue vitriol*, *blue stone*, *blue copperas*, or sulphate of copper, have been already mentioned as formed in the preparation of sulphurous acid (p. 199), by dissolving copper in oil of vitriol, a process which is occasionally

employed for the manufacture of this salt. A considerable supply of the sulphate is obtained as a secondary product in the process of silver-refining (p. 210).

The sulphate of copper is also manufactured by roasting copper pyrites ($FeCuS_2$) with free access of air, when it becomes partly converted into a mixture of sulphate of copper with sulphate of iron, $FeCuS_2 + O_8 = FeO.SO_3 + CuO.SO_3$.

The sulphate of iron, however, is decomposed by the heat, losing its sulphuric acid, and leaving simply peroxide of iron (see p. 321). When the roasted mass is treated with water, the oxide of iron is left undissolved, but the sulphate of copper enters into solution, and may be obtained in crystals by evaporation.

These crystals, as they are found in commerce, are usually opaque, but if they are dissolved in hot water and allowed to crystallise slowly, they become perfectly transparent, and have then the composition expressed by the formula $CuO.SO_3.5H_2O$. If the crystals be heated to the temperature of boiling water, they lose four-fifths of their water, and crumble down to a greyish white powder, which has the composition $CuO.SO_3.H_2O$, and if this be moistened with water, it becomes very hot and resumes its original blue colour. The whitish opacity of the ordinary crystals of blue stone is due to the absence of a portion of the water of crystallisation.

The fifth molecule of water can be expelled only at a temperature of nearly 400° F., and is therefore generally called water of constitution (see p. 41), the formula of the crystals being then written $CuO.SO_3.H_2O.4Aq$. The crystals dissolve in four parts of cold and two parts of boiling water. The solution reddens litmus.

The sulphate of copper is largely employed by the dyer and calico-printer, and in the manufacture of pigments. It is also occasionally used in medicine, in the electrotype process, and in galvanic batteries.

If a solution of sulphate of copper be mixed with an excess of solution of potash, a blue precipitate of *hydrated oxide of copper* ($CuO.H_2O$) is produced. On boiling this in the liquid, it loses its water and becomes black oxide. The paint known [illegible]*verditer* is hydrated oxide of copper obtained by decomposin[illegible] [illegible]nner with hydrate of lime.

When ammonia is added to [illegible] a basic sulphate is first precipitated, which is diss[illegible] [illegible] to a dark blue fluid. On allowing this to evapora[illegible] [illegible] *ammonio-sulphate of copper*, $CuO.SO_3, 4NH_3, H_2O$, are dep[illegible] [illegible] lose their ammonia when exposed to the air.

A *basic sulphate of copper*, $CuO.SO_3, 4(CuO.H_2O)$, constitutes the mineral *brochantite*.

Sulphate of copper cannot easily be separated by crystallisation from the sulphates of iron, zinc, and magnesia, because it forms double salts with them, which contain, like those sulphates, 7 molecules of water. An instance of this is seen in the *black vitriol* obtained from the mother-liquor of the sulphate of copper at Mansfeld, and forming bluish black crystals isomorphous with green vitriol, $FeO.SO_3.7H_2O$. The formula of black vitriol may be written, $(CuMgFeMnCoNi)\,O.SO_3.7H_2O$, the six isomorphous metals being interchangeable without altering the general character of the salt.

Arsenite of copper or Scheele's green has been mentioned at p. 244.

The basic *phosphates of copper* compose the minerals *tagalite* and *libethenite.*

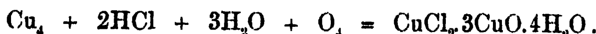
The basic *carbonates of copper* have been noticed as forming the very beautiful minerals *blue malachite,* or *chessylite,* and *green malachite.*

Mineral green ($CuO.CO_2$, $CuO.H_2O$) has the same composition as green malachite, and is prepared by mixing hot solutions of carbonate of soda and sulphate of copper. When boiled in the liquid, it is gradually converted into black oxide of copper.

Silicates of copper are found in the minerals *dioptase,* or *emerald copper,* and *chrysocolla.*

244. *Chlorides of copper.*—The chloride of copper (*cupric chloride*) ($CuCl_2$) is produced by the direct union of its elements, when it forms a brown mass, which fuses easily, and is decomposed into chlorine and subchloride of copper, the latter being afterwards converted into vapour. When dissolved in water, it gives a solution which is green when concentrated, and becomes blue on dilution. The hydrated chloride of copper is readily prepared by dissolving the black oxide in hot hydrochloric acid, and allowing the solution to crystallise; it forms green needle-like crystals ($CuCl_2.2H_2O$). A solution of chloride of copper in alcohol burns with a splendid green flame, and the chloride imparts a similar colour to a gas flame.

Oxychloride of copper ($CuCl_2.3CuO.4H_2O$) is found at Atacama, in prismatic crystals, and is called *atacamite.* The paint *Brunswick green* has the same composition, and is made by moistening copper with solution of hydrochloric acid or of sal-ammoniac, and exposing it to the air in order that it may absorb oxygen—



$$Cu_4 + 2HCl + 3H_2O + O_4 = CuCl_2.3CuO.4H_2O.$$

The Brunswick green of the shops frequently consists of a mixture of Prussian blue, chromate of lead, and sulphate of baryta.

Subchloride of copper (*cuprous chloride*), Cu_2Cl_2, is formed when fine copper turnings are shaken with strong hydrochloric acid in a bottle of air ($Cu_2 + 2HCl + O = Cu_2Cl_2 + H_2O$). The subchloride dissolves in the excess of [illegible] brown solution from which water [illegible] [illegible]r, for this is one of the f[illegible] When exposed to light, it assumes a [illegible] be obtained in larger quantity by dissolving [illegible] black oxide of copper in hydrochloric acid, and boiling with [illegible] fine copper turnings, the brown solution being afterwards precipitated by water. If the solution be moderately diluted and set aside, it deposits tetrahedral crystals of the subchloride. Ammonia (free from air) dissolves the subchloride to a colourless liquid, which becomes dark-blue by contact with air, absorbing oxygen. The ammoniacal solution of subchloride of copper is employed as a test for acetylene (p. 89), which gives a red precipitate with it. The solution may be preserved in a colourless state by keeping it in a well-stoppered bottle, quite full, with strips of clean copper. When copper, in a finely divided state, is boiled with solution of hydrochlorate of ammonia, the solution deposits colourless crystals of the salt $Cu_2Cl_2(NH_3)_2$. If the solution of this salt be exposed to the air, blue crystals are deposited, having the formula $Cu_2Cl_2.(NH_3)_2CuCl_2.(NH_3)_2H_2O$, and on further exposure, a compound of this last salt with hydrochlorate of ammonia is deposited. The solu-

tion of subchloride of copper in hydrochloric acid is employed for absorbing carbonic oxide in the analysis of gaseous mixtures (p. 251). When this solution is exposed to air it absorbs oxygen, and deposits the oxychloride of copper. A strong solution of hydrochlorate of ammonia or of chloride of potassium readily dissolves the cuprous chloride, even in the cold, forming soluble double chlorides. The solution in chloride of potassium does not absorb oxygen quite so easily as that in hydrochlorate of ammonia.

245. *Sulphides of copper.*—Copper has a very marked attraction for sulphur, even at the ordinary temperature. A bright surface of copper soon becomes tarnished by contact with sulphur, and hydrosulphuric acid blackens the metal. Finely divided copper and sulphur combine slowly at the ordinary temperature, and when heated together, they combine with combustion. A thick copper wire burns easily in vapour of sulphur (p. 193). Copper is even partly converted into sulphide when boiled with sulphuric acid, as in the preparation of sulphurous acid gas. This great attraction of copper for sulphur is taken advantage of in the process of *kernel-roasting* for extracting the copper from pyrites containing as little as 1 per cent. of the metal. The pyrites is roasted in large heaps (p. 190) for several weeks, when a great part of the iron is converted into peroxide, and the copper remains combined with sulphur, forming a hard kernel in the centre of the lumps of ore. This kernel contains about 5 per cent. of copper, and can be smelted with economy. Children are employed to detach the kernel from the shell, which consists of peroxide of iron and a little sulphate of copper, which is washed out with water.

The *subsulphide of copper* (Cu_2S) has been mentioned among the ores of copper, and among the furnace products in smelting, when it is sometimes obtained in octahedral crystals. It is not attacked by hydrochloric acid, but nitric acid dissolves it readily. *Copper pyrites* is believed to contain the copper in the form of subsulphide, its true formula being $Cu_2S.Fe_2S_3$; for if the copper be pre[illegible] sulphide, CuS, the iron must be present as protosulphide, and th[illegible] would have the formula CuS.FeS. Now, FeS is easil[illegible] sulphuric or hydrochloric acid, which is not [illegible] acid, however, attacks it violently.

Sulphide of copper (CuS) occurs in nature [illegible] *copper*, and may be obtained as a black precipitate [illegible] hydrosulphuric acid upon solution of sulphate of copper. [illegible] precipitate is boiled with sulphur and hydrosulphate of ammonia, it is dissolved in small quantity, and the solution on cooling deposits fine scarlet needles containing a higher sulphide of copper combined with hydrosulphate of ammonia.

A *pentasulphide of copper* (CuS_5) is obtained by decomposing sulphate of copper with pentasulphide of potassium; it forms a black precipitate, distinguished from the other sulphides of copper by its solubility in carbonate of potash.

The sulphides of copper, when exposed to air in the presence of water, are slowly oxidised and converted into sulphate of copper, which is dissolved by the water. It appears to be in this way that the *blue water* of the copper mines is formed.

Phosphide of copper (Cu_4P_2), obtained as a black powder by boiling

solution of sulphate of copper with phosphorus, has been already mentioned as a convenient source of phosphuretted hydrogen. Another phosphide, obtained by passing vapour of phosphorus over finely divided copper at a high temperature, is employed in Abel's composition for magneto-electric fuzes, in conjunction with subsulphide of copper and chlorate of potash.

Silicon may be made to unite with copper by strongly heating finely divided copper with silicic acid and charcoal. A bronze-like mass is thus obtained, containing about 5 per cent. of silicon. It is said to rival iron in ductility and tenacity, and fuses at about the same temperature as bronze.

LEAD.

Pb″ = 207 parts by weight.

246. Lead owes its usefulness in the metallic state chiefly to its softness and fusibility. The former quality allows it to be easily rolled into thin sheets, and to be drawn into the form of tubes or pipes; it is indeed the softest of the metals in common use, and, at the same time, the least tenacious, so that it can only be drawn with difficulty into thin wire, and is then very easily broken. The ease with which it makes a dark streak upon paper shows how readily minute particles of the metal may be abraded. Its want of elasticity also recommends it for some special uses, as for deadening a shock or preventing a rebound.

In fusibility it surpasses all the other metals commonly employed in the metallic state, except tin, for it melts at 617° F., and this circumstance, taken in conjunction with its high specific gravity (11·4), particularly adapts it for the manufacture of shot and bullets. For one of its extensive uses, however, as a covering for roofs, it would be better suited if it were lighter and less fusible, for in case of fire in houses so roofed, the fall of the molten lead frequently aggravates the calamity.

With the exception, perhaps, of the ores of iron, none is more abundant in this country than th[illegible]e of lead, *galena*, a sulphide of lead (PbS). This ore mi[illegible] glance be mistaken for the metal itself, from i[illegible] and metallic lustre. It is found formi[illegible] [illegible]umberland, Derbyshire, and Cornwall, [illegible] in the two first counties, and a clay slate in [illegible] Spain al[illegible] furnishes large supplies of this important ore. [illegible] presents a beautiful crystalline appearance, being often found in large isolated cubes, which readily cleave or split up in directions parallel to their faces. Blende (sulphide of zinc) and copper pyrites (sulphide of copper and iron) are frequently found in the same vein with galena, and it is usually associated with quartz (silica), heavy-spar (sulphate of baryta), or fluor spar (fluoride of calcium). Considerable quantities of sulphide of silver are often present in galena, and in many specimens the sulphides of bismuth and antimony are found.

Though the sulphide is the most abundant natural combination of lead, it is by no means the only form in which this metal is found. The metal itself is occasionally met with, though in very small quantity, and the carbonate of lead ($PbO.CO_2$), *white lead ore*, forms an important ore in the United States and in Spain. The sulphate of lead ($PbO.SO_3$) is also found in Australia, and is largely imported into this country to be smelted.

247. The extraction of lead from galena is effected by taking advantage of the circumstance, that when a combination of a metal with oxygen is raised to a high temperature in contact with a sulphide of the same metal, the oxygen and sulphur unite, and the metal is liberated.

The ore, having been separated by mechanical treatment as far as possible from the foreign matters associated with it, is mixed with a small proportion of lime, and spread over the hearth of a reverberatory furnace (fig. 259), the sides of which are considerably inclined towards the centre, so as to form a hollow for the reception of the molten lead.

During the first stage of the smelting process, the object is to roast the ore with free access of air, exposing as large a surface as possible,

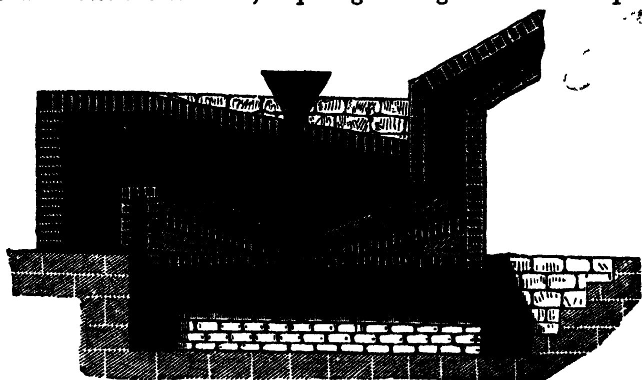
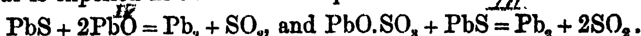


Fig. 259.—Furnace for smelting lead-ores.

on which account the heat is kept below that at which galena fuses; indeed, during the first two hours, no fuel is thrown into the grate, sufficient heat being radiated from the sides of the furnace, which have become red hot during the smelting of the previous charge of ore. The ore is stirred from time to time, to ex[illegible] fresh surfaces to the action of the atmospheric oxygen.

The effect of this roasting is to con[illegible] the sulphide of lead (PbS) into sulphate of lead (PbO.S[illegible]), [illegible] portion loses its sulphur, which is evolved as sulphurous ac[illegible] and [illegible] oxygen in its stead, becoming converted into oxide [illegible] (P[illegible]). [illegible] proportion of the galena, however, remains unoxidised. [illegible]ing is sufficiently advanced, some fuel is thrown into the grate, [illegible] slags from previous smeltings are thrown on to the hearth, the damper [illegible] slightly raised, and the doors of the furnace are closed, so that the charge may be heated to the temperature at which the oxide and sulphate of lead act upon the unaltered sulphide, furnishing metallic lead, whilst the sulphur is expelled in the form of sulphurous acid:



$$PbS + 2PbO = Pb_3 + SO_2, \text{ and } PbO.SO_3 + PbS = Pb_2 + 2SO_2.$$

During this part of the operation, the contents of the hearth are constantly raked up towards the fire-bridge, so as to facilitate the separation of the lead, and to cause it to run down into the hollow provided for its reception. It is also found that the separation of the lead from the slags is much assisted by occasionally throwing open the doors to chill the furnace. After about four hours, the charge is reduced to a pretty fluid condition, the lead having accumulated at the bottom

of the depressed portion of the hearth with the slag above it; this slag consists chiefly of the silicates of lime and oxide of lead, and would have contained a larger proportion of the latter, if the lime had not been added as a flux at the commencement of the operation.* In order still further to reduce the quantity of lead in the slag, a few more shovelfuls of lime are now thrown into the hearth, together with a little small coal, the latter serving to reduce to the metallic state the oxide of lead displaced by the lime from its combination with the silicic acid.

But since silicate of lime is far less fusible than silicate of oxide of lead, the effect of this addition of lime is to "dry up" the slags to a semi-solid mass, and it will now be seen that if the whole of the lime had been added at the commencement of the smelting, the diminished fusibility of the slag would have opposed an obstacle to the separation of the metallic lead.

During the last hour or so, the temperature is very considerably raised, and at the expiration of about six hours, when the greater portion of the lead is thought to have separated, the slag is raked out through one of the doors of the furnace, and the melted metal allowed to run out through a tap-hole in front of the lowest portion of the hearth, into an iron basin, from which it is ladled into pig-moulds.

The rich slags, together with the layer of subsulphide of lead (Pb_2S) which forms over the surface of the metal, are worked up again with a fresh charge of ore.

In the smelting of galena, a very considerable quantity of lead is carried off in the form of vapour; and in order to condense this, the gases from the furnace are made to pass through flues, the aggregate length of which is sometimes three or four miles, before being allowed to escape up the chimney. When these flues are swept, many tons of lead are recovered in the forms of oxide and sulphide.

In the north of England, the smelting of lead ores is now generally conducted in an *economico-furnace* (fig. 260), or small blast-furnace, instead of the reverberatory furnace described above. Air is supplied to the furnace through three blast-pipes (A), and the lead-ore and fuel being charged in at B, the lead runs into a cavity (C) at the bottom of the furnace, whilst the slag flows over into a reservoir (D) outside the furnace. The charge is sprinkled with water through the rose (E) fixed just above the opening into the chimney (F), to prevent it from being blown away by the current of air.



Fig. 260.

248. Some varieties of lead, particularly those smelted from Spanish ores, are known as *hard lead*, their hardness being chiefly due to the presence of antimony, and since this hardness interferes materially with some of the uses of the metal, such lead is generally subjected to an *improving* or *cal-*

cining process, in which the impurities are oxidised and removed, together with a portion of the lead, in the dross.* To effect this, six or eight tons of the hard lead are fused in an iron pot (P, fig. 261), and transferred to a shallow cast-iron pan (C) measuring about ten feet by five. In this pan, which is set in the hearth of a reverberatory furnace, and is about eight inches deep nearest the grate, and nine inches at the other end, the lead is kept in fusion by the flame which traverses it from the grate G to the flue F, for a period varying with the degree of impurity, some specimens being found sufficiently soft after a single day's calcination, whilst others must be kept in a state of fusion for three or four weeks. The workman judges of the progress of the operation by a peculiar flaky crystalline appearance assumed by a small sample on cooling. When sufficiently purified, the metal is run off and cast into pigs.

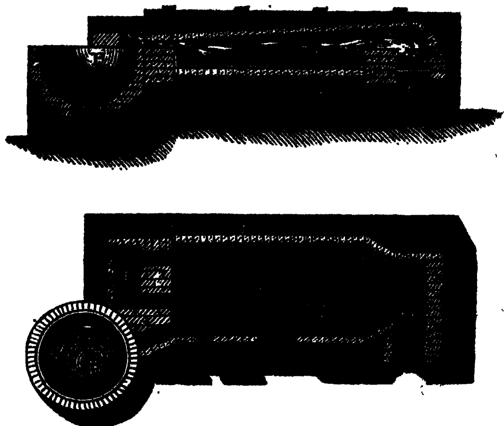


Fig. 261.

At first sight, it is not intelligible how antimony should be removed from lead by calcination, since lead is the more easily oxidised metal. The result must be ascribed to the tendency of antimony to form antimonic acid (Sb_2O_5) which combines with the oxide of lead. The dross (antimoniate of lead) formed in this process, when reduced to the metallic state, yields an alloy of lead with 30 [illegible] per cent. of antimony, which is much used for casting type furnit[illegible] printers.

249. *Extraction of silver from* [illegible] lead [illegible] galena often contains a sufficient quantity of silver t[illegible] extracted. Previously to the year 1829, this was [illegible] the lead contained more than 11 oz. of silver per ton, [illegible] then known for effecting the separation of the two metals was [illegible] cupellation, which necessitates the conversion of the whole of the lead int[illegible] oxide, which has then to be separated from the silver and again reduced

* The following analyses illustrate the composition of hard lead:—

	English.	Spanish.
Lead,	99·27	95·81
Antimony,	0·57	3·66
Copper,	0·1	0·32
Iron,	0·04	0·21
	100·00	100·00

to the metallic state, thus consuming so large an amount of labour, that a considerable yield of silver must be obtained to pay for it.

By the simple and ingenious operation known as *Pattinson's desilverising process*, a very large amount of the lead can be at once separated in the metallic state with little expenditure of labour, thus leaving the remainder sufficiently rich in the more precious metal to defray the cost of the far more expensive process of cupellation, so that 3 or 4 oz. of silver per ton can be extracted with profit. Pattinson founded his process upon the observation that when lead containing a small proportion of silver is melted and allowed to cool, being constantly stirred, a considerable quantity of the lead separates in the form of crystals containing a very minute proportion of silver, almost the whole of this metal being left behind in the portion still remaining liquid.

Eight or ten cast-iron pots, set in brickwork, each capable of holding [illegible] lead, are placed in a row, with a fire-place underneath each [illegible] (fig. 262). Suppose that there are ten pots numbered consecu-

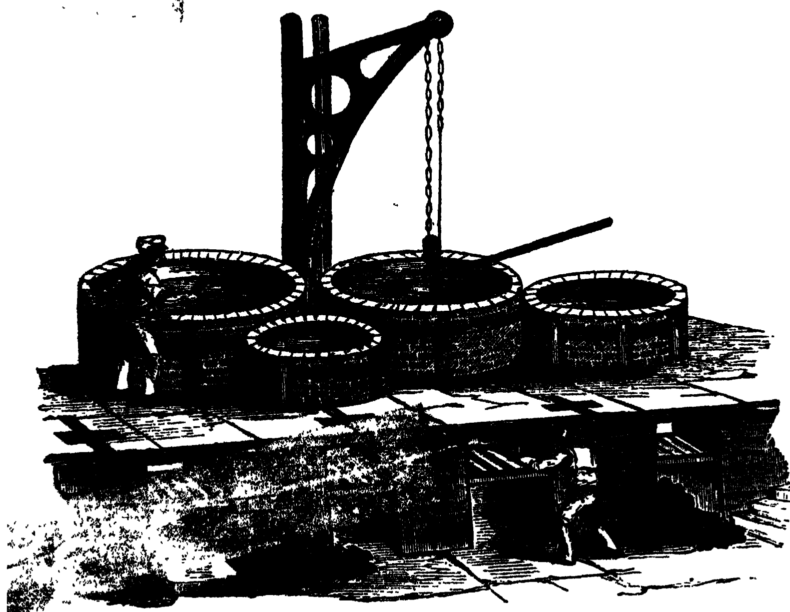
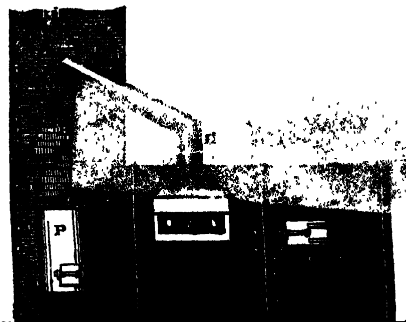


Fig. 262.—Pattinson's desilverising process.

tively, that on the extreme left of the workman being No. 1, and that on his extreme right No. 10. About 6 tons of the lead containing silver are melted in pot No. 5, the metal skimmed, and the fire raked out from beneath so that the pot may gradually cool, its liquid contents being constantly agitated with a long iron stirrer. As the crystals of lead form, they are well drained in a perforated ladle (about 10 inches wide and 5 inches deep) and transferred to pot No. 4. When about $\frac{4}{6}$ths of the metal have thus been removed in the crystals, the portion still remaining liquid, which retains the silver, is ladled into pot No. 6, and the pot

No. 5, which is now empty, is charged with fresh argentiferous lead to be treated in the same manner.

When pots Nos. 4 and 6 have received, respectively, a sufficient quantity of the crystals of lead and of the liquid part rich in silver, their contents are subjected to a perfectly similar process, the crystals of lead being always passed to the left, and the rich argentiferous alloy to the right. As the final result of these operations, the pot No. 10, to the extreme right, becomes filled with a rich alloy of lead and silver, sometimes containing 300 ounces of silver to the ton, whilst pot No. 1, to the extreme left, contains lead in which there is not more than ¼ ounce of silver to the ton. This lead is cast into pigs for the market. The ladle used in the above operation is kept hot by a small *temper pot* containing melted lead. A fulcrum is provided at the edge of each pot, for resting the ladle during the shaking of the crystals to drain off the liquid metal. Any copper present in the lead is also left with the silver in the liquid portion.



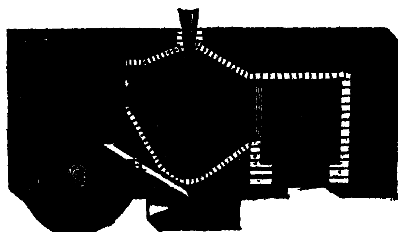


Fig. 263.—Cupellation furnace.

250. In order to extract the silver from the rich alloy, it is subjected to a process of refining, or *cupellation*, which is founded upon the oxidation suffered by lead when heated in air, and upon the absence of any tendency on the part of silver to combine directly with oxygen.

The refinery or cupelling furnace (fig. 263), in which this operation is performed, is a reverberatory furnace, the hearth of which consists of a *cupel* (C), made by ramming moist powdered bone-ash mixed with a little wood-ash into an oval iron frame about 4 inches deep, and provided with four cross-bars at the bottom, each about 4 inches wide. When this frame has been well filled with bone-ash, part of it is scooped out, so as to leave the sides about two inches thick at the top, and three inches at the bottom, the bone-ash being left about one inch thick above the iron cross-bars.

The cupel, which is about 4 feet long by 2½ feet wide, is fixed so that the flame from the grate (G) passes across it into the chimney (B), and at one end, the nozzle (N) of a blowing apparatus directs a blast of air over the surface of the contents of the cupel. The latter is carefully dried by a gradually increasing heat, and is then heated to redness; the alloy of lead and silver, having been previously melted in an iron pot (P) fixed by the side of the furnace, is ladled in through a gutter, until the cupel is nearly filled with it; a film of oxide soon makes its appearance upon the surface of the lead, and is fused by the high temperature. When the blast is directed upon the surface, it blows off this film of

oxide, and supplies the oxygen for the formation of another film upon the clean metallic surface thus exposed. A part of the oxide of lead or litharge thus formed is at first absorbed by the porous material of the cupel, but the chief part of it is forced by the blast through a channel cut for the purpose in the opposite end to that at which the blast enters, and is received, as it issues from A, in an iron vessel placed beneath the furnace.

In proportion as the lead is in this manner removed from the cupel, fresh portions are supplied from the adjoining melting-pot, and the process is continued until about 5 tons of the alloy have been added.

The cupellation is not continued until the whole of the lead has been removed, but until only 2 or 3 cwts. of that metal are left in combination with the whole of the silver (say 1000 ounces) contained in the 5 tons of alloy. The metal is run through a hole made in the bottom of the cupel, which is then again stopped up so that a fresh charge may be introduced.

The fumes of oxide of lead which are freely evolved during this process are carried off by a hood and chimney (H) situated opposite to the blast of air.

When three or four charges have been cupelled, so as to yield from 3000 to 5000 ounces of silver, alloyed with 6 or 8 cwts. of lead, the removal of the latter metal is completed in another cupel, since some of the silver is carried off with the last portions of litharge.

The appearances indicating the removal of the last portion of lead are very striking; the surface of the molten metal, which has been hitherto tarnished, becomes iridescent as the film of oxide of lead thins off, and afterwards resplendently bright, and when the cake of refined silver is allowed to cool, it throws up from its surface a variety of fantastic arborescent excrescences, caused by the escape of oxygen which has been mechanically absorbed by the fused silver, and is given off during solidification.

The litharge obtained from the cupelling furnaces is reduced to the metallic state by mixing it with small coal, and heating it in a furnace similar to that employed in smelting galena.

251. On the small scale, lead may easily be extracted from galena by mixing 300 grains with 450 grains of dried carbonate of soda and 20 grains of charcoal, introducing the mixture into a crucible, and placing in it two tenpenny nails, heads downwards. The crucible is covered and heated in a moderate fire for about half an hour. (A charcoal fire in the small furnace, fig. 132, p. 114, will suffice.) The remainder of the nails is carefully removed from the liquid mass, which is then allowed to cool, the crucible broken, and the lead extracted and weighed. In this process the sulphur of the galena is removed, partly by the sodium of the carbonate, and partly by the iron of the nails, the excess of carbonate of soda serving to flux any silica with which the galena may be mixed.

To ascertain if it contains silver, the button is placed in a small bone-ash cupel (fig. 264), heated in a muffle (fig. 265) until the whole of the lead is oxidised, and absorbed into the bone-ash of the cupel, leaving the minute globule of silver.

Small globules of lead may be conveniently cupelled on charcoal before the blowpipe, by pressing some bone-ash into a cavity scooped in the charcoal, placing the lead upon its surface, and exposing it to a good oxidising flame (p. 105) as long as it decreases in size. If any copper be present, the bone-ash will show a green stain after cooling. Pure lead gives a yellow stain.

252. *Uses of lead.*—The employment of this metal for roofing, &c., has been already noticed. Its fusibility adapts it for casting type for

printing, but it would be far too soft for this purpose; accordingly, *type-metal* consists of an alloy of 4 parts of lead with 1 of antimony. A similar alloy is used for the bullets contained in shrapnel shells, since bullets of soft lead would be liable to be jammed together, and would not scatter so well on the explosion of the shell. On the other hand, rifle bullets are made of very pure soft lead, in order that they may more easily take the grooves of the rifle.



Fig. 264.

Small shot are made of lead to which about 40 lbs. of arsenic per ton has been added. The arsenic dissolves in the lead, hardening it and causing it to form spherical drops when chilled. The fluid metal is poured through a sort of colander fixed at the top of a lofty tower (or at the mouth of a deserted coal-shaft), and the minute drops into which it is thus divided are allowed to fall into a vessel of water, after having been chilled by the air in their descent. They are afterwards sorted, and polished in revolving barrels containing plumbago. If too little arsenic is employed, the shot are elongated or pyriform; and if the due proportion has been exceeded, their form is flattened or lenticular.

Common solder is an alloy of equal weights of lead and tin, which is more fusible than either metal separately. Other alloys containing lead will be noticed in their proper places.

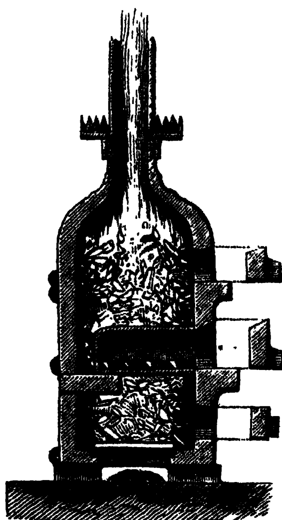


Fig. 265.

Leaden vessels are much used in manufacturing chemistry, on account of the resistance of this metal to the action of acids. Neither concentrated sulphuric, hydrochloric, nitric, or hydrofluoric acid, will act upon lead at the ordinary temperature. The best solvent for the metal is nitric acid of sp. gr. 1·2, since the nitrate of lead, being insoluble in an acid of greater strength, would be deposited upon the metal, which it would protect from further action.

Lead is easily corroded in situations where it is brought in contact with air highly charged with carbonic acid, when it absorbs oxygen, forming oxide of lead, which combines with carbonic acid and water to produce the basic carbonate of lead ($PbO.CO_2,PbO.H_2O$). The lead of old coffins is often found converted into a white earthy-looking brittle mass of basic carbonate, with a very thin film of metallic lead inside it.

When lead is exposed to the joint action of air and the acetic acid contained in beer, wine, cider, &c., it becomes converted into acetate of lead or sugar of lead, which is very poisonous. Hence the accidents arising from the reprehensible practice of sweetening cider by keeping it in contact with lead, and from the accidental presence, in beer and wine bottles, of shot which have been employed in cleaning them. The action of water upon leaden cisterns has been already noticed. Contact with air and sea-water soon converts lead into oxide and chloride.

253. Oxides of lead.—Four compounds of lead with oxygen are known—

Suboxide of lead,	Pb_2O
Oxide ,,	PbO
Red oxide ,,	Pb_3O_4
Peroxide ,,	PbO_2.

The bright surface of lead soon tarnishes when exposed to the air, becoming coated with a dark film, which is believed to consist of suboxide of lead. In a very finely divided state, lead takes fire when thrown into the air, and is converted into oxide of lead.

The *lead pyrophorus*, for exhibiting the spontaneous combustion of lead, is prepared by placing some tartrate of lead in a glass tube closed at one end (fig. 266), drawing the tube out to a narrow neck near the open end, and holding it nearly horizontally, whilst the tartrate of lead is heated with a gas or spirit flame as long as any fumes are evolved; the neck is then fused with a blowpipe flame and drawn off. The tartrate of lead ($PbO.C_4H_4O_5$), when heated, leaves a mixture of metallic lead with charcoal, which prevents it from fusing into a compact mass. This mixture may be preserved unchanged in the tube for any length of time; but when the neck is broken off and the contents scattered into the air, they inflame at once, producing thick fumes of oxide of lead. Tartrate of lead is prepared by adding ammonia to solution of tartaric acid constantly stirred, until the precipitate of bitartrate of ammonia at first formed is just redissolved, and precipitating the liquid with solution of acetate of lead. The precipitated tartrate of lead is collected upon a filter, washed several times, and dried at a gentle heat.


Fig. 266.

Oxide or *protoxide of lead* is prepared on a large scale by heating lead in air. When the metal is only moderately heated, the oxide forms a yellow powder, which is known in commerce as *massicot*, but at a higher temperature the oxide melts, and on cooling forms a brownish scaly mass which is called *litharge* (λίθος, *stone*; ἄργυρος, *silver*), probably because that obtained by the alchemists would always furnish a considerable proportion of silver, which was present in most samples of lead before the introduction of Pattinson's process. The litharge of commerce often has a red colour, caused by the presence of some red oxide of lead; from 1 to 3 per cent. of finely divided metallic lead may also sometimes be found in it. When heated to dull redness, litharge assumes a dark brown colour, and becomes yellow on cooling. At a bright red heat it fuses, and readily attacks clay crucibles, forming a fusible silicate of lead, and soon perforating the sides. When boiled with distilled water, litharge is dissolved in small quantity, yielding a solution which is decidedly alkaline, and becomes turbid when exposed to the air, absorbing carbonic acid, and depositing carbonate of lead. The presence of a small quantity of saline matter in the water hinders the solution of the oxide, but organic matter, and especially sugar, favours it. Two definite white *hydrates of oxide of lead*, $H_2O.2PbO$ and $H_2O.3PbO$, may be obtained by precipitating solutions of lead with the alkalies. Oxide of lead is a powerful base, and has a strong tendency to form basic salts. Hot solutions of potash and soda dissolve it readily, and deposit it in pink crystals on cooling.

Litharge, from its easy combination with silicic acid at a high tempera-

ture, is much used in the manufacture of glass, and in glazing earthenware. The assayer also employs it as a flux. A mixture of litharge with lime is sometimes applied to the hair, which it dyes of a purplish-black colour, due to the formation of sulphide of lead from the sulphur existing in hair. *Dhil mastic*, used by builders in repairing stone, is a mixture of 1 part of massicot with 10 parts of brickdust, and enough linseed oil to form a paste; it sets into a very hard mass, which is probably due partly to the formation of silicate of lead, and partly to the *drying* of the linseed oil by oxidation favoured by the oxide of lead.

Red lead or *minium* is prepared by heating massicot in air to about 600° F., when it absorbs oxygen, and becomes converted into red lead. The massicot for this purpose is prepared by heating lead in a reverberatory furnace to a temperature insufficient to fuse the oxide which is formed, and rejecting the first portions, which contain iron and other metals more easily oxidisable than lead (as cobalt), as well as the last, which contain copper and silver, less easily oxidised than lead. The intermediate product is ground to a fine powder and suspended in water; the coarser particles are thus separated from the finer, which are dried, and heated on iron trays placed in a reverberatory furnace, till the requisite colour has been obtained. Minium is largely used in the manufacture of glass, whence it is necessary that it should be free from the oxides of iron, copper, cobalt, &c., which would colour the glass. It is also employed as a common red mineral colour, and in the manufacture of lucifer-matches.

When minium is treated with dilute nitric acid, nitrate of lead ($PbO.N_2O_5$), or $Pb(NO_3)_2$, is obtained in solution, and peroxide of lead (PbO_2) is left as a brown powder, showing that minium is probably a compound of the oxide and peroxide of lead. The minium obtained by heating massicot in air till no further increase of weight is observed, has the composition $2PbO.PbO_2$, or Pb_3O_4, which would appear to represent pure minium; commercial minium, however, has more frequently a composition corresponding to $3PbO.PbO_2$, but when this is treated with potash, PbO is dissolved out, and $2PbO.PbO_2$ remains. Minium evolves oxygen at a red heat, becoming PbO, hence the necessity for keeping the temperature below 600° F. during its preparation.

Peroxide, or *binoxide*, or *puce oxide of lead*, is found in the mineral kingdom as *heavy lead ore*, forming black, lustrous, six-sided prisms. It may be prepared from red lead by boiling it, in fine powder, with nitric acid, diluted with five measures of water, washing and drying. The binoxide of lead easily imparts oxygen to other substances; sulphur, mixed with it, may be ignited by friction, hence this oxide is a common ingredient in lucifer-match compositions. Its oxidising property is frequently turned to account in the laboratory, for example, in absorbing sulphurous acid from gaseous mixtures by converting it into sulphate of lead; $PbO_2 + SO_2 = PbO.SO_3$. Binoxide of lead is not dissolved by dilute acids and has no basic properties; indeed, it is sometimes called plumbic acid, for it combines with potash and soda when fused with their hydrates. Plumbate of potash ($K_2O.PbO_2.3H_2O$) has been crystallised from an alkaline solution, but is decomposed by pure water.

254. *White lead* or *ceruse* is a carbonate of oxide of lead, or, strictly speaking, a basic carbonate, a combination of carbonate of oxide of lead ($PbO.CO_2$) with variable proportions of hydrated oxide of lead ($PbO.H_2O$). This substance is a constant product of the corrosive action

of air and water upon the metal. Its formation is, of course, very much encouraged by the presence of organic matters in a state of decay, which evolve carbonic acid.

White lead is manufactured on the large scale by two processes, which depend, however, upon the same principle; this may be stated as follows :— When oxide of lead is brought in contact with acetic acid ($H.C_2H_3O_2$), it forms the acetate of lead (sugar of lead, $Pb(C_2H_3O_2)_2$). This salt is capable of combining with two molecules of oxide of lead, forming the tribasic acetate of lead, $Pb(C_2H_3O_2)_2.2PbO$, and if this be acted upon by carbonic acid, the oxide of lead is converted into carbonate, whilst the neutral acetate of lead, $Pb(C_2H_3O_2)_2$, is left.

In the older of the two processes, commonly known as the Dutch process, metallic lead, in the form of square gratings cast from the purest lead, is placed over earthen pots containing a small quantity of common vinegar; a number of these pots being built up into heaps, together with alternate layers of dung or spent tan, the heaps are entirely covered up with the same material. The metal is thus exposed to conditions most favourable to its oxidation, viz., a very warm and moist atmosphere produced by the fermentation of the organic matters composing the heap, and the presence of a large quantity of acid vapour generated from the acetic acid of the vinegar. The lead is therefore soon converted into oxide, a portion of which unites with the acetic acid to form the tribasic acetate of lead, which is then decomposed by the carbonic acid devolved from the fermenting dung or tan, yielding carbonate of lead, which combines with another portion of the oxide of lead and of water to form the white lead. The neutral acetate of lead left after the removal of the oxide of lead from the tribasic acetate, is now ready to take up an additional quantity of the oxide, and the process is thus continued until, in the course of a few weeks, the lead has become coated with a very thick crust of white lead; the heaps are then destroyed, the crust detached, washed, to remove adhering acetate of lead, ground to a paste with water, and dried. Rolled lead is not so easily converted as cast lead.

The newer process is a more direct application of the same principle, for it consists in boiling acetic acid with an excess of litharge in order to produce the tribasic acetate of lead, which is afterwards decomposed by passing through it a current of carbonic acid obtained by combustion or fermentation, or even by exhalation from the earth. The solution of neutral acetate of lead is then again boiled with litharge, when tribasic acetate is produced, and is again precipitated by the carbonic acid. The precipitated carbonate of lead always carries down with it a variable proportion of the hydrated oxide of lead. This process is, of course, much more rapid than the old one, and dispenses with the grinding, which is so injurious to the workmen; but the white lead so produced, being crystalline, has less opacity or covering-power (*body*) than that obtained by the Dutch method.

The usual composition of white lead is expressed by the formula $PbO.H_2O, 2(PbO.CO_2)$, though other basic carbonates of lead are often mixed with it.

White lead being very poisonous, its use by painters and others is generally attended with symptoms of lead-poisoning, arising in many cases, probably, from neglecting to wash the hands before eating, the effect of lead being *cumulative*, so that minute doses may show their combined action after many days. Diluted sulphuric acid and solutions of the sul-

phates of magnesia and the alkalies are sometimes taken internally to counteract its effect, since the sulphate of lead is not poisonous.

All paints containing lead, and cards glazed with white lead, are blackened even by minute quantities of sulphuretted hydrogen, from the production of black sulphide of lead. If the blackened surface remain exposed to the light and air, it is bleached again, the sulphide of lead (PbS) being oxidised and converted into white sulphate of lead ($PbO.SO_3$), but this does not take place in the dark. A little sulphide of lead or powdered charcoal is sometimes mixed with commercial white lead to give it a bluish tint.

The pure *carbonate of lead* is found in white crystals associated with galena.

Sulphate of lead is found in nature in prismatic and octahedral crystals of *anglesite* or *lead-vitriol*. It is nearly insoluble in diluted acids, and is one of the chief forms in which lead is precipitated from its solutions in analytical operations. The minerals *lanarkite* and *leadhillite* are compounds of sulphate and carbonate of lead. The chromates of lead have been already noticed.

Phosphate of lead ($3PbO.P_2O_5$) is occasionally associated with the carbonate in the ores of lead.

255. *Chloride of lead* ($PbCl_2$) forms the mineral termed *horn-lead*. It is one of the few chlorides which are not readily soluble in water, and is precipitated when hydrochloric acid or a soluble chloride is added to a solution of lead. Boiling water dissolves about $\frac{1}{30}$ of its weight of chloride of lead, and deposits it in beautiful shining white needles on cooling. It fuses easily, and is converted into vapour at a high temperature.

The *oxychloride of lead* ($PbCl_2.PbO$) is formed when chloride of lead is heated in air. It is sometimes employed as a substitute for white lead in painting, being prepared for this purpose by decomposing finely powdered galena with concentrated hydrochloric acid ($PbS + 2HCl = PbCl_2 + H_2S$), washing the resulting chloride of lead with cold water, dissolving it in hot water, and adding lime-water, which precipitates the oxychloride—



$$2PbCl_2 + CaO = PbCl_2.PbO + CaCl_2 .$$

Turner's yellow (Paris yellow, patent yellow, mineral yellow) is another oxychloride of lead ($PbCl_2.7PbO$), prepared by heating a mixture of litharge and sal-ammoniac. It has a fine golden yellow colour, is easily fused, and crystallises in octahedra on cooling. The mineral *mendipite* is an oxychloride of lead ($PbCl_2.2PbO$) which occurs in colourless prismatic crystals.

Iodide of lead (PbI_2) is obtained as a bright yellow precipitate on mixing solutions of nitrate or acetate of lead and iodide of potassium. If it be allowed to settle, the liquid poured off, and the precipitate dissolved in boiling water (with one or two drops of hydrochloric acid), it forms a colourless solution, depositing golden scales as it cools.

256. *Sulphides of lead.*—The subsulphide (Pb_2S) has been mentioned as produced in smelting galena. Sulphide of lead, or galena, has been described among the ores of lead. It is always obtained as a black precipitate when hydrosulphuric acid or a soluble sulphide acts upon a solution containing lead, even in minute proportion.

A persulphide of lead, the composition of which has not been ascer-

tained, is formed as a red precipitate when a solution of lead is mixed with a solution of an alkaline sulphide saturated with sulphur (or with solution of hydrosulphate of ammonia which has been kept till it has acquired a red colour).

Chlorosulphide of lead ($3PbS.2PbCl_2$) is obtained as a bright red precipitate when hydrosulphuric acid is added in small quantity to a solution of chloride of lead in hydrochloric acid.

Selenide of lead (PbSe) occurs associated with the sulphide in some lead ores; it much resembles galena, and has the same crystalline form.

257. Thallium (Tl = 204 parts by weight).—The discovery of this metal in 1861 was one of the first results of the application of the new method of testing by observation of coloured lines in the spectrum of a flame, described at p. 272. Crookes was examining the spectrum obtained by holding in the flame of a Bunsen burner the deposit formed in the flues of a sulphuric acid chamber, in which pyrites was employed as the source of sulphur. A green line made its appearance in the spectrum, which a less acute and practised observer might have mistaken for one of the lines caused by barium (see fig. 238), with which it nearly coincides in position; but the line was much brighter than that produced by barium, and on instituting a searching analysis of the deposit, a metal was obtained which did not agree in properties with any hitherto described, and was named *thallium*, from θαλλός, *a young shoot*, in allusion to the vernal green colour of its spectrum line. It has since been detected in several mineral waters; but the pyrites obtained from Spain and Belgium appear to be its best source. From the flue-dust of the sulphuric acid chambers, the metal is extracted by a simple process, but large quantities must be operated on to obtain any considerable amount. The deposit is treated with boiling water, and the solution mixed with much strong hydrochloric acid, which precipitates the thallium as chloride; this is converted into acid sulphate of thallium by treatment with sulphuric acid, and this salt having been purified by recrystallisation, is decomposed by zinc, which precipitates metallic thallium in a spongy form, fusible into a compact mass in an atmosphere of coal-gas.

In external characters thallium is very similar to lead; but it tarnishes much more rapidly when exposed to air, and the streak which it makes on paper soon becomes yellowish, being converted into oxide of thallium. If a tarnished piece of the metal be allowed to touch the tongue, a strongly alkaline taste is perceived, for the oxide of thallium or *thallous oxide* (Tl_2O) is very soluble in water, so that the tarnished metal becomes bright when immersed in water. The ready solubility of the oxide seemed to require thallium to be classed among the alkali-metals, a view which was encouraged by the circumstance that its specific heat proved it to be monatomic like potassium and sodium. But thallium appears to be more nearly related to another monatomic metal, silver, by the sparing solubility of its chloride and the insolubility of its sulphide. The circumstance that it may be kept unaltered in water, and may be precipitated from its salts by zinc, at once removes it from the group of alkali-metals. The ready solubility of its oxide in water is only an exaggeration of the behaviour of the oxides of lead and silver, both of which dissolve slightly in water, yielding alkaline solutions. Diluted sulphuric acid acts upon thallium as upon zinc, evolving hydrogen. Thallium burns in oxygen with a beautiful green flame, and the chlorate of thallium has been recommended for the manufacture of green fires in place of chlorate of baryta (see p. 164). The sulphate of thallium, unlike that of lead, is easily soluble in water; the carbonate is rather sparingly soluble, but far more soluble than carbonate of lead.

Thallic oxide, Tl_2O_3, is obtained by adding hypochlorite of soda to thallous chloride mixed with excess of carbonate of soda. It is also a basic oxide, its sulphate having the composition $Tl_2O_3.3SO_3.H_2O.6Aq$.

Salts of thallium, like those of lead, are poisonous.

The equivalent and atomic weights of thallium appear to be identical, and are expressed by the number 204.

SILVER.

Ag' = 108 parts by weight.

258. In silver, we meet with the first metal hitherto considered which is not capable of undergoing oxidation in the air, under any circumstances, and this, in conjunction with its beautiful appearance, occasions its manifold ornamental uses, which are much favoured also by the great malleability and ductility of this metal (in which it ranks only second to gold), for the former property enables it to be rolled out into thin plates or leaves, so that a small quantity of silver suffices to cover a large surface, whilst its ductility permits the wire-drawer to produce that extremely thin silver wire which is employed in the manufacture of silver lace.

Silver, although pretty widely diffused, is found in comparatively small quantity, and hence it bears a high value, which adapts it for a medium of currency.

As might be expected from its want of direct attraction for oxygen, silver is found frequently in the metallic or native state, crystallised in cubes or octahedra, which are sometimes aggregated together, as in the silver-mines of Potosi, into arborescent or *dendritic* forms. Silver is more frequently met with, however, in combination with sulphur, forming the sulphide of silver (Ag_2S), which is generally associated with large quantities of the sulphides of lead, antimony, and iron. The largest supplies of silver are obtained from the Mexican and Peruvian mines, but the quantity furnished by Saxony and Hungary is by no means insignificant.

The process by which silver is extracted from galena has been already described under the history of lead.

The ores of copper (particularly the grey copper-ore) often contain so much silver as to be worth working for that metal, in which case they are smelted in the usual way, when the copper obtained is found to contain the whole of the silver present in the ore. This silver is separated from the copper by taking advantage of the facility with which the former metal is dissolved by melted lead. The process of *liquation*, as it is termed, consists in fusing the argentiferous copper with about thrice its weight of lead, and casting the alloy thus obtained into cakes or discs, which are afterwards gradually heated upon a hearth (fig. 267), so contrived that the lead, which melts much more easily than the copper, may flow off in the liquid state, carrying with it, in the form of an alloy, the silver which was associated with the copper, leaving this last metal in porous masses, having the form of the original disks, upon the hearth. The lead and silver are separated by the process of cupellation (p. 351).

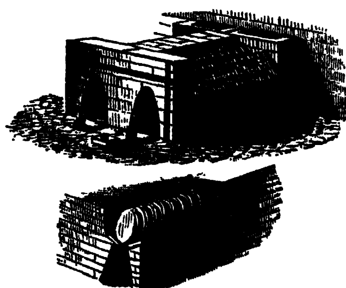


Fig 267.—Liquation hearth.

When the extraction of the silver is the main object with which a particular ore is treated, the process of *amalgamation* is adopted, in which the silver is dissolved out by means of mercury. At Freiberg, the silver is extracted by this method from an ore which contains sulphide of silver together with much iron pyrites and other metallic sulphides. The ore is mixed with a small proportion of common salt, and roasted in a rever-

beratory furnace, when the sulphide of silver is converted into chloride of silver. It is then ground to a very fine powder, which is agitated, in revolving casks, with water and metallic iron, when the latter appropriates the chlorine and reduces the silver to the metallic state. A quantity of mercury is then introduced into the casks, and the revolution continued for several hours; the mercury dissolves the silver, copper, and lead, and is run out of the barrels into stout linen strainers, which allow the excess of fluid mercury to pass through, but retain the soft solid amalgam containing the silver. In order to recover the silver, this amalgam is placed in iron trays arranged one above the other (fig. 268), and covered with an iron bell-shaped receiver standing over water. By heaping burning fuel round the upper part of this dome, its temperature is raised sufficiently to convert the mercury into vapour, which condenses again in the water, leaving the silver, together with the copper and lead, upon the iron trays. Finally, the silver is refined by fusing it with an additional quantity of lead and subjecting the alloy to cupellation (p. 351), when the fused oxide of lead which is formed carries with it the copper, also in the form of oxide, leaving the silver in a state of purity.

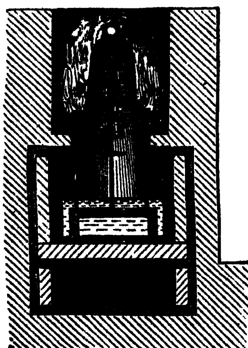


Fig. 268.

Various methods have been devised to supersede the amalgamation process. For example, the ores have been roasted with common salt to convert the silver into chloride, which is dissolved out of the mass by means of a strong solution of common salt, from which the silver is afterwards precipitated in the metallic state by copper. Hyposulphite of soda has also been employed to dissolve out the chloride of silver, and the solution precipitated by sulphide of sodium, the resulting sulphide of silver being roasted to remove the sulphur and leave metallic silver.

Although silver is capable of resisting the oxidising action of the atmosphere, it is liable to considerable loss by wear and tear in consequence of its softness, and is therefore always hardened, for useful purposes, by the addition of a small proportion of copper. The *standard silver* employed for coinage and for most articles of silver plate, in this country, contains, in 1000 parts, 925 of silver and 75 of copper, whilst that used in France contains 900 of silver and 100 of copper.

Standard silver, for coining and other purposes, is whitened by being heated in air and immersed in diluted sulphuric acid, which dissolves out the oxide of copper, leaving a superficial film of nearly pure silver. *Dead* or *frosted* silver is produced in this manner. *Oxidised silver* is covered with a thin film of sulphide by immersion in a solution obtained by boiling sulphur with potash.

The solder employed in working silver consists of 5 parts of silver, 2 of zinc, and 6 of brass.

Plated articles are manufactured from copper or one of its alloys, which has been united by rolling with a thin plate of silver, the adhesion of the latter being promoted by first washing the surface of the copper with a solution of nitrate of silver, when a film of this metal is deposited upon its surface, the copper taking the place of the silver in the solution.

Electro-plating consists in covering the surface of baser metals with a coating of silver, by connecting them with the negative (or zinc) pole of the galvanic battery, and immersing them in a solution made by dissolving cyanide of silver in cyanide of potassium; * the current gradually decomposes the cyanide of silver, and this metal is of course (see p. 6) deposited upon the object connected with the negative pole, whilst the cyanogen liberated at the positive (copper or platinum) pole is allowed to act upon a silver plate with which this pole is connected, so that the silvering solution is always maintained at the same strength, the quantity of silver dissolved at this pole being precisely equal to that deposited at the opposite pole.

Brass and copper are sometimes silvered by rubbing them with a mixture of 10 parts of chloride of silver with 1 of corrosive sublimate (chloride of mercury) and 100 of bitartrate of potash. The silver and mercury are both reduced to the metallic state by the baser metal, and an amalgam of silver is formed, which readily coats the surface. The acidity of the bitartrate of potash promotes the reduction. The surface to be silvered should always be cleansed from oxide by momentary immersion in nitric acid, and washed with water. For *dry silvering*, an amalgam of silver and mercury is applied to the clean surface, and the mercury is afterwards expelled by heat.

Silvering upon glass is effected by means of certain organic substances which are capable of precipitating metallic silver from its solutions. Looking-glasses have been made by pouring upon the surface of plates of glass a solution containing tartrate of silver and tartrate of ammonia. On heating the glass plates to a certain temperature, the oxide of silver contained in the tartrate parts with its oxygen to the tartaric acid, and the metallic silver is deposited in a closely adhering film. Glass globes and vases are silvered internally by a process which is exactly similar in principle.

Pure silver is easily obtained from standard silver by dissolving it in nitric acid, with the aid of heat, diluting the solution with water, adding solution of common salt as long as it produces any fresh precipitate of chloride of silver, washing the precipitate by decantation as long as the washings give a blue tinge with ammonia, and fusing the dried precipitate with half its weight of dried carbonate of soda in a brisk fire, when a button of silver will be found on breaking the crucible—



$$2AgCl + Na_2O.CO_2 = Ag_2 + 2NaCl + O + CO_2.$$

259. *Properties of silver.*—The brilliant whiteness of silver distinguishes it from all other metals. It is lighter than lead, its specific gravity being 10·53; harder than gold, but not so hard as copper; more malleable and ductile than any other metal except gold, which it surpasses in tenacity. It fuses at a somewhat lower temperature than gold or copper (about 1870° F.), and is the best conductor of heat and electricity. It is not oxidised by dry or moist air, either at the ordinary or at high temperatures, but is oxidised by ozone, and tarnished by air containing sulphuretted hydrogen, from the production of sulphide of silver, which is easily removed by solution of cyanide of potassium. It is unaffected by dilute acids, with the exception of nitric; but hot concentrated sulphuric acid converts it into sulphate of silver, and when boiled with strong hydrochloric acid, it dissolves to a slight extent in the form of chloride of

* A solution of cyanide of potassium in 10 parts of water, with 50 grains of chloride of silver dissolved in each pint of the liquid, will answer the purpose.

silver, which is precipitated on adding water. The hydrates of potash and soda do not act on silver to the same extent as on platinum when fused with it; hence silver basins and crucibles are much used in the laboratory.

260. *Oxides of silver.*—There are three compounds of silver with oxygen: the suboxide, Ag_4O; the oxide, Ag_2O; and the peroxide, probably Ag_2O_2, which is not known in the pure state. The oxide alone has any practical interest, as being the base contained in the salts of silver with oxygen-acids.

Oxide of silver (Ag_2O) is obtained as a brown precipitate when solution of nitrate of silver is decomposed by potash. It is a powerful base, slightly soluble in water, to which it imparts a weak alkaline reaction. A moderate heat decomposes it into its elements. When moist, freshly precipitated oxide of silver is covered with a strong solution of ammonia, and allowed to stand for some hours, it becomes black, and acquires dangerously explosive properties. The composition of this *fulminating silver* is not accurately known, but it is supposed to be a nitride of silver, NAg_3, corresponding in composition to ammonia.

Nitrate of silver ($Ag_2O.N_2O_5$, or $AgNO_3$), or *lunar caustic* (silver being distinguished as *luna* by the alchemists), is procured by dissolving silver in nitric acid, with the aid of a gentle heat, evaporating the solution to dryness, and heating the residue till it fuses, in order to expel the excess of acid. For use in surgery, the fused nitrate is poured into cylindrical moulds, so as to cast it into thin sticks; but for chemical purposes it is dissolved in water and crystallised, when it forms colourless square tables. The action of nitrate of silver as a caustic depends upon the facility with which it parts with oxygen, the silver being reduced to the metallic state, and the oxygen combining with the elements of the organic matter. This effect is very much promoted by exposure to sunlight or diffused daylight. Pure nitrate of silver is not changed by exposure to light, but if organic matter be present, a black deposit, containing finely divided silver, is produced. Thus, the solution of nitrate of silver stains the fingers black when exposed to light, but the stain may be removed by cyanide of potassium. If solution of nitrate of silver be dropped upon paper, and exposed to light, black stains will be produced, and the paper corroded. Nitrate of silver is a frequent constituent of marking inks, since the deposit of metallic silver formed on exposure to light is not removable by washing. The linen is sometimes *mordanted* by applying a solution of carbonate of soda before the marking ink, when the insoluble carbonate of silver is precipitated in the fibre, and is more easily blackened than the nitrate, especially if a hot iron is applied. Marking inks without preparation are made with nitrate of silver containing an excess of ammonia, which appropriates the nitric acid, and hastens the blackening on exposure to light or heat. Hair dyes often contain nitrate of silver. The important use of this salt in photography has been noticed already (p. 214).

In order to prepare nitrate of silver from standard silver (containing copper), the metal is dissolved in moderately strong nitric acid, and the solution evaporated to dryness in a porcelain dish, when a blue residue containing the nitrates of silver and copper is obtained. The dish is now moderately heated until the residue has fused, and become uniformly black, the blue nitrate of copper being decomposed, and leaving black oxide of copper, at a temperature which is insufficient to decompose the nitrate of silver. To ascertain when all the nitrate of copper is decomposed, a small

sample is removed on the end of a glass rod, dissolved in water, filtered, and tested with ammonia, which will produce a blue colour if any nitrate of copper is left. The residue is treated with hot water, the solution filtered from the oxide of copper, and evaporated to crystallisation.

261. *Chloride of silver* (AgCl) is an important compound, as being the form into which silver is commonly converted in extracting it from its ores, and in separating it from other metals. It separates as a white curdy precipitate, when solution of hydrochloric acid or a chloride is mixed with a solution containing silver. The precipitate is brilliantly white at first, but soon becomes violet, and eventually black, if exposed to daylight, or more rapidly in sunlight, the chloride of silver being reduced to subchloride (Ag_2Cl), with separation of chlorine (see p. 214). The blackening takes place more rapidly in the presence of an excess of nitrate of silver or of organic matter, upon which the liberated chlorine is capable of acting. The chloride of silver, formed by suspending silver leaf in a bottle of chlorine gas, is not blackened by light. If the white chloride of silver be dried in the dark, and heated in a crucible, it fuses at about 500° F. to a brownish liquid, which solidifies, on cooling, to a transparent, nearly colourless mass, much resembling horn in external characters (*horn silver*); a strong heat converts it into vapour, but does not decompose it. If fused chloride of silver be covered with hydrochloric acid, and a piece of zinc placed upon it, it will be found entirely reduced, after a few hours, to a cake of metallic silver; the first portion of silver having been reduced in contact with the zinc, and the remainder by the galvanic action set up by the contact of the two metals beneath the acid. Ammonia readily dissolves chloride of silver, and the solution deposits colourless crystals of the chloride when evaporated. If the ammonia be very strong, the solution deposits a crystalline compound of chloride of silver with ammonia. The absorption of ammoniacal gas by chloride of silver has been noticed at p. 123, and the photographic application of the chloride at p. 214.

Recovery of silver from old photographic baths.—One of the simplest methods of effecting this consists in mixing the liquid with solution of common salt as long as it causes a fresh precipitate of chloride of silver, which is allowed to subside, washed once or twice by decantation, mixed with a little sulphuric acid, a lump of zinc (spelter) placed in it, and left for a day or two to reduce the silver to the metallic state. The zinc is then taken out, and the metallic silver well washed by decantation, first, with dilute sulphuric acid, to remove zinc, and afterwards with water, till the washings are quite tasteless. It may either be reconverted into nitrate by dissolving in nitric acid (p. 362), or fused in an earthen crucible with a little borax.

From the fixing solutions containing hyposulphite of soda, the silver cannot be precipitated by salt, because the chloride of silver is soluble in the hyposulphite. A piece of sheet copper left in this for a day or two will precipitate the silver at once in the metallic state.

Subchloride of silver (Ag_2Cl) has been obtained by the action of perchloride of iron upon metallic silver ($Ag_4 + Fe_2Cl_6 = 2Ag_2Cl + 2FeCl_2$). It is black and insoluble in nitric acid. Ammonia decomposes it, dissolving out chloride of silver, and leaving metallic silver.

Bromide of silver (AgBr) is a rare Chilian mineral. Associated with chloride of silver, it forms the mineral *embolite*. It much resembles the chloride, but is somewhat less easily dissolved by ammonia.

Iodide of silver (AgI) is also found in the mineral kingdom. It is worthy of remark that silver decomposes hydriodic acid much more easily than hydrochloric acid, forming iodide of silver, and evolving hydrogen.

The iodide of silver dissolves in hot hydriodic acid, and is deposited in crystals on cooling. By adding nitrate of silver to iodide of potassium, the iodide of silver is obtained as a yellow precipitate which, unlike the chloride, does not dissolve in ammonia. Iodide of silver dissolves in a boiling saturated solution of nitrate of silver, and the solution, on cooling, deposits crystals having the composition $AgI.AgNO_3$, which are far more sensitive to the action of light than iodide of silver itself, a circumstance which is taken advantage of by photographers. The crystals are decomposed by water, with separation of iodide of silver.

Sulphide of silver (Ag_2S) is found as *silver glance*, which may be regarded as the chief ore of silver; it has a metallic lustre, and is sometimes found in cubical or octahedral crystals. The minerals known as *rosiclers* or *red silver ores* contain sulphide of silver combined with the sulphides of arsenic and antimony. The black precipitate obtained by the action of hydrosulphuric acid upon a solution of silver is the sulphide of silver. It may also be formed by heating silver with sulphur in a covered crucible. Sulphide of silver is remarkable for being soft and malleable, so that medals may even be struck from it. It is not dissolved by diluted sulphuric or hydrochloric acid, but nitric acid readily dissolves it. Metallic silver dissolves sulphide of silver when fused with it, and becomes brittle even when containing only 1 per cent. of the sulphide.

MERCURY.

$Hg'' = 200$ parts by weight.*

262. Mercury (*quicksilver*) is the only metal which is liquid at the ordinary temperature, and since it requires a temperature of 39° below zero F. to solidify it, this metal is particularly adapted for the construction of thermometers and barometers. Its high boiling point (662° F.) also recommends it for the former purpose, as does its high specific gravity (13·54) for the latter, a column of about 30 inches in height being able to counterpoise a column of atmospheric air having the same sectional area, and a height equal to that of the atmosphere above the level of the sea. The symbol for mercury (Hg) is derived from the Latin name for this element, *hydrargyrum* (ὕδωρ, *water*, referring to its fluidity, ἄργυρον, *silver*).

Mercury is not met with in this country, but is obtained from Idria (Austria), Almaden (Spain), China, and New Almaden (California). It occurs in these mines partly in the metallic state, diffused in minute globules or collected in cavities, but chiefly in the state of cinnabar, which is a sulphide of mercury (HgS).

The metal is extracted from the sulphide at Idria by roasting the ore in a kiln (fig. 269), which is connected with an extensive series of condensing chambers built of brick-work. The sulphur is converted, by the air in the kiln, into sulphurous acid gas, whilst the mercury passes off in vapour and condenses in the chambers.

At Almaden the extraction is conducted upon the same principle, but the condensation of the mercury is effected in earthen receivers (called

* The vapour of mercury is only 100 times as heavy as hydrogen, which would indicate 100 as the atomic weight of mercury, but the specific heat of mercury when multiplied by 100 would give an atomic heat only half that of most other metals.

aludels) opening into each other, and delivering the mercury into a gutter which conveys it to the receptacles.

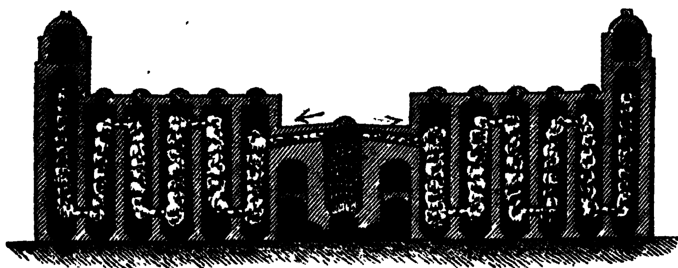


Fig. 269.—Extraction of mercury at Idria.

The cinnabar is placed upon the arch (A, fig. 270) of brick-work, in which there are several openings for the passage of the flame of the wood fire kindled at B; this flame ignites the sulphide of mercury, which burns in the air passing up from below, forming sulphurous acid gas and vapour of mercury ($HgS + O_2 = Hg + SO_2$), which escape through the flue (F) into the aludels (C), where the chief part of the mercury condenses, and runs down into the gutter (G). The sulphurous acid gas escapes through the flue (H), and any mercury which may have escaped condensation is collected in the trough (D), the gas finally passing out through the chimney (E), which provides for the requisite draught.

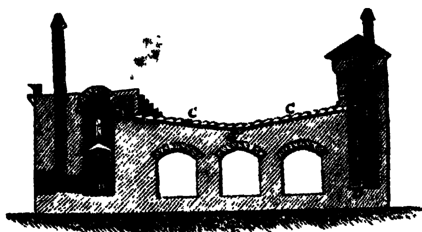


Fig. 270.

In the Palatinate, the cinnabar is distilled in cast-iron retorts with lime, when the sulphur is left in the residue as sulphide of calcium, and sulphate of lime, whilst the mercury distils over—



$$4HgS + 4CaO = 3CaS + CaO.SO_3 + Hg_4.$$

The mercury found in commerce is never perfectly pure, as may be shown by scattering a little upon a clean glass plate, when it *tails* or leaves a track upon the glass, which is not the case with pure mercury. Its chief impurity is lead, which may be removed by exposing it in a thin layer to the action of nitric acid diluted with two measures of water, which should cover its surface, and be allowed to remain in contact with it for a day or two, with occasional stirring. The lead is far more easily oxidised and dissolved than the mercury, though a little of this also passes into solution. The mercury is afterwards well washed with water and dried, first with blotting-paper, and then by a gentle heat. Mercury is easily freed from mechanical impurities by filtering it through a cone of paper, round the apex of which a few pin-holes have been made.

263. Although mercury in its ordinary condition is not oxidised by air at the ordinary temperature, it appears to undergo a partial oxidation when reduced to a fine state of division, as in those medicinal preparations of the metal which are made by triturating it with various substances which have no chemical action upon it, until globules of the metal are no longer visible. *Blue pill* and *grey powder*, or *hydrargyrum cum*

cretâ, afford examples of this, and probably owe much of their medicinal activity to the presence of one of the oxides of mercury.

264. *Uses of mercury.*—One of the chief uses to which mercury is devoted is the *silvering of looking-glasses*, which is effected by means of an amalgam of tin in the following manner: a sheet of tin-foil of the same size as the glass to be silvered is laid perfectly level upon a table, and rubbed over with metallic mercury, a thin layer of which is afterwards poured upon it. The glass is then carefully slid on to the table, so that its edge may carry before it part of the superfluous mercury with the impurities upon its surface; heavy weights are laid upon the glass so as to squeeze out the excess of mercury, and in a few days the combination of tin and mercury is found to have adhered firmly to the glass; this coating usually contains about 1 part of mercury and 4 parts of tin. In this and all other arts in which mercury is used (such as barometer-making) much suffering is experienced by the operatives, from the poisonous action of the mercury.

The readiness with which mercury unites with most other metals to form *amalgams* is one of its most striking properties, and is turned to account for the extraction of silver and gold from their ores. The attraction of the latter metal for mercury is seen in the readiness with which it becomes coated with a silvery layer of mercury, whenever it is brought in contact with that metal, and if a piece of gold leaf be suspended at a little distance above the surface of mercury, it will be found, after a time, silvered by the vapour of the metal which rises slowly even at the ordinary temperature. From the surface of rings which have been accidentally whitened by mercury, it may be removed by a moderate heat, or by warm dilute nitric acid, but the gold will afterwards require burnishing.

Zinc plates are *amalgamated*, as it is termed, for use in the galvanic battery, by rubbing the liquid metal over them under the surface of dilute sulphuric acid, which removes the coating of oxide from the surface of the zinc. The amalgam of zinc is not acted on by the diluted sulphuric acid used in the battery (see p. 4) until the *circuit* is completed, so that no zinc is wasted when the battery is not in use. An amalgam of 6 parts of mercury with 1 part of zinc and 1 of tin is also used to promote the action of electrical machines.

The addition of a little amalgam of sodium to metallic mercury gives it the power of adhering much more readily to other metals, even to iron. Such an addition has been recommended in all cases where metallic surfaces have to be amalgamated, and especially in the extraction of silver and gold from their ores by means of mercury.

Iron and platinum are the only metals in ordinary use which can be employed in contact with mercury without being corroded by it. Mercury, however, adheres to platinum.

The following definite compounds of mercury with other metals have been obtained by combining them with excess of mercury, and squeezing out the fluid metal by hydraulic pressure, amounting to 60 tons upon the inch:—

Amalgam of lead,	Pb_2Hg	Amalgam of zinc,	Zn_2Hg
,, silver,	$AgHg$	,, copper,	$CuHg$
,, iron,	$FeHg$	,, platinum,	$PtHg_2$.

The amalgam of silver ($AgHg$) has been found in nature, in dodecahedral crystals.

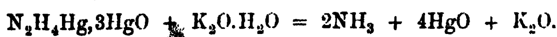
A very beautiful crystallisation of the amalgam of silver (*Arbor Dianæ*) may be obtained in long prisms having the composition Ag_2Hg_3, by dissolving 400 grains of nitrate of silver in 40 measured ounces of water, adding 160 minims of concentrated nitric acid, and 1840 grains of mercury; in the course of a day or two crystals of 2 or 3 inches in length will be deposited.

265. *Oxides of mercury.*—Two oxides of mercury are known, the suboxide Hg_2O, and the oxide HgO; both combine with acids to form salts.

Suboxide of mercury, black oxide or *mercurous oxide* (Hg_2O), is obtained by decomposing calomel with solution of potash, and washing with water ($2HgCl + K_2O = Hg_2O + 2KCl$). It is very easily decomposed by exposure to light or to a gentle heat, into oxide of mercury and metallic mercury.

Red oxide of mercury or *mercuric oxide* (HgO), is formed upon the surface of mercury, when heated for some time to its boiling point in contact with air. The oxide is black while hot, but becomes red on cooling. It is used, under the name of *red precipitate*, in ointments, and is prepared for this purpose by dissolving mercury in nitric acid, evaporating the solution to dryness, and gently calcining the nitrate of mercury ($HgO.N_2O_5$) until the nitric acid is expelled. The name *nitric oxide of mercury* refers to this process. It is thus obtained, after cooling, as a brilliant red crystalline powder, which becomes nearly black when heated, and is resolved into its elements at a red heat. It dissolves slightly in water, and the solution has a very feeble alkaline reaction. A bright yellow modification of the oxide is precipitated when a solution of corrosive sublimate is decomposed by potash ($HgCl_2 + K_2O = HgO + 2KCl$); the yellow variety is chemically more active than the red.

When oxide of mercury is acted on by strong ammonia, it becomes converted into a yellowish white powder which possesses the properties of a strong base, absorbing carbonic acid eagerly from the air, and combining readily with other acids. It is easily decomposed by exposure to light, and, if rubbed in a mortar when dry, is decomposed with slight detonations, a property in which it feebly resembles fulminating silver (p. 362). The composition of this substance is represented by the formula $4HgO.2NH_3.2H_2O$, and it is sometimes called *ammoniated oxide of mercury.* When exposed *in vacuo* over oil of vitriol, it loses $2H_2O$, becoming $4HgO.2NH_3$, but if heated to about 260° F., it becomes brown;* it now contains $Hg_4O_3N_2H_4$, and may be regarded as a compound of oxide of mercury with two molecules of ammonia in which two atoms of hydrogen are displaced by mercury ($N_2H_4Hg'',3HgO$), a view which would explain, in a simple manner, the evolution of ammonia when the substance is fused with hydrate of potash—

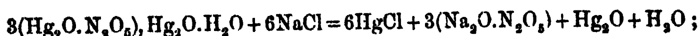


$$N_2H_4Hg,3HgO + K_2O.H_2O = 2NH_3 + 4HgO + K_2O.$$

This substance is sometimes called *mercuramine;* it forms salts with the acids; the *sulphate of mercuramine* has the composition $(N_2H_4Hg,3HgO)SO_3$.

By passing ammonia gas over the yellow oxide of mercury as long as it is absorbed, and heating the compound to about 260° F. in a current of ammonia as long as any water is evolved, a brown explosive powder is obtained, which is believed to be a *nitride of mercury*, N_2Hg_3'', representing a double molecule of ammonia in which the hydrogen has been displaced by mercury. It yields salts of ammonia when decomposed by hydrated acids.

266. The salts formed by the oxides of mercury with the oxygen-acids are not of great practical importance. *Protonitrate of mercury* or *mercurous nitrate* is obtained when mercury is dissolved in nitric acid diluted with five volumes of water; it may be procured in crystals having the composition $Hg_2O.N_2O_5,2Aq$. The prismatic crystals which are sometimes sold as protonitrate of mercury consist of a basic nitrate, $3(Hg_2O.N_2O_5),Hg_2O.H_2O$, prepared by acting with diluted nitric acid upon mercury in excess. When this salt is powdered in a mortar with a little common salt, it becomes black from the separation of suboxide of mercury—



$$3(Hg_2O.N_2O_5),Hg_2O.H_2O + 6NaCl = 6HgCl + 3(Na_2O.N_2O_5) + Hg_2O + H_2O;$$

* It has been stated that by heating it for some time in a current of dry ammonia, the whole of the oxygen may be expelled as water, leaving the oxide of mercurammonium $(NHg_2'')_2O$, which is very explosive, and combines with water to form a hydrate which produces salts with the acids.

but the neutral nitrate is not blackened ($Hg_2O.N_2O_5 + 2NaCl = 2HgCl + Na_2O.N_2O_5$). These nitrates cannot be dissolved in water without partial decomposition and precipitation of yellow basic nitrates.

Nitrate of mercury or *mercuric nitrate* is formed when mercury is dissolved with an excess of strong nitric acid, and the solution boiled. It is better to prepare it by saturating strong nitric acid, diluted with an equal measure of water, with oxide of mercury. It may be obtained in crystals of the formula $2(HgO.N_2O_5),Aq$. Water decomposes it, precipitating a yellow basic nitrate, which leaves oxide of mercury when long washed with water.

Sulphate of suboxide of mercury or *mercurous sulphate* ($Hg_2O.SO_3$) is precipitated as a white crystalline powder when dilute sulphuric acid is added to a solution of protonitrate of mercury.

Sulphate of mercury or *mercuric sulphate* ($HgO.SO_3$) is obtained by heating 2 parts by weight of mercury with 3 parts of oil of vitriol, and evaporating to dryness. Mercurous sulphate is first produced, and is oxidised by the excess of sulphuric acid. It forms a white crystalline powder, which is decomposed by water into a soluble acid sulphate, and an insoluble yellow basic sulphate of mercury, $HgO.SO_3.2HgO$, known as *turbith* or *turpeth* mineral, said to have been so named from its resembling in its medicinal effects the root of the *Convolvulus turpethum*.

267. CHLORIDES OF MERCURY.—The chlorides are the most important of the compounds of mercury, the chloride being *calomel* ($HgCl$) and the bichloride, *corrosive sublimate* ($HgCl_2$). Vapour of mercury burns in chlorine gas, corrosive sublimate being produced.*

Corrosive sublimate, chloride of mercury, bichloride or *perchloride of mercury*, or *mercuric chloride*, is manufactured by heating 2 parts by weight of mercury with 3 parts of strong sulphuric acid, and evaporating to dryness, to obtain mercuric sulphate ($Hg + 2(H_2O.SO_3) = HgO.SO_3 + 2H_2O + SO_2$), which is mixed with 1½ part of common salt and heated in glass vessels ($HgO.SO_3 + 2NaCl = Na_2O.SO_3 + HgCl_2$), when sulphate of soda is left, and the corrosive sublimate is converted into vapour, condensing on the cooler part of the vessel in lustrous colourless masses, which are very heavy (sp. gr. 5·4), and have a crystalline fracture. It fuses very easily (at 509° F.) to a perfectly colourless liquid, which boils at 563° F., emitting an extremely acrid vapour, which destroys the sense of smell for some time. This vapour condenses in fine needles, or sometimes in octahedra. Corrosive sublimate dissolves in three times its weight of boiling water, but requires 16 parts of cold water, so that the hot solution readily deposits long four-sided prismatic crystals of the salt. It is remarkable that alcohol and ether dissolve corrosive sublimate much more easily than water, boiling alcohol dissolving about an equal weight of the chloride, and cold ether taking up one-third of its weight. By shaking the aqueous solution with ether, the greater part of the corrosive sublimate will be removed, and will remain dissolved in the ether which rises to the surface. Water in which sal-ammoniac has been dissolved will take up corrosive sublimate more easily than pure water, a soluble double chloride (*sal alembroth*) being formed, which may be obtained in tabular crystals of the composition $HgCl_2.6NH_4Cl, H_2O$. A solution of corrosive sublimate in water containing sal-ammoniac is a very efficacious *bug-poison*.

The poisonous properties of corrosive sublimate are very marked, so little as three grains having been known to cause death in the case of a child. The white of egg is commonly administered as an antidote, because it is known to form an insoluble compound with corrosive sublimate, so as to render the poison inert in the stomach. The compound of albumen

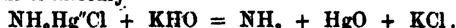
* 2 vols. of vapour of corrosive sublimate contain 2 vols. of mercury vapour (see note to page 364) and 2 vols. of chlorine.

with corrosive sublimate is also much less liable to putrefaction than albumen itself, and hence corrosive sublimate is sometimes employed for preserving anatomical preparations and for preventing the decay of wood (by combining with the vegetable albumen of the sap).

Chloride of mercury unites with many other chlorides to form soluble double salts, and with oxide of mercury, forming several *oxychlorides of mercury*, which have no useful applications.

White precipitate, employed for destroying vermin, is deposited when a solution of corrosive sublimate is poured into an excess of solution of ammonia; $HgCl_2 + 2NH_3 = NH_3.HCl + \underset{\text{White precipitate.}}{NH_2Hg''Cl}$

The true constitution of white precipitate has been the subject of much discussion, but the changes which it undergoes, under various circumstances, appear to lead to the conclusion that it represents hydrochlorate of ammonia, $NH_3.HCl$, in which half of the hydrogen has been displaced by mercury. When boiled with potash, it yields ammonia and oxide of mercury—



$$NH_2Hg''Cl + KHO = NH_3 + HgO + KCl.$$

If it be boiled with water, it is only partly decomposed in a similar manner, leaving a yellow powder having the composition $(NH_2HgCl).HgO$, produced according to the equation—



$$2(NH_2HgCl) + H_2O = NH_3.HCl + \underset{\text{Yellow precipitate.}}{(NH_2HgCl).HgO}.$$

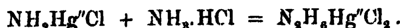
A compound corresponding to this yellow precipitate, but containing chloride of mercury in place of the oxide, is precipitated when ammonia is gradually added to solution of corrosive sublimate in large excess, the result being a compound of white precipitate with a molecule of undecomposed chloride of mercury,—



$$(NH_2HgCl).HgCl_2.$$

If white precipitate be heated to about 600° F., it evolves ammonia, and yields a sublimate of ammoniated chloride of mercury, $HgCl_2.NH_3$, leaving a red crystalline powder which is insoluble in water and in diluted acids, and is unchanged by boiling with potash; it may be represented as a compound of bichloride of mercury with ammonia, in which the whole of the hydrogen has been displaced by mercury, $N_2Hg_3''.2HgCl_2$.

When solution of corrosive sublimate is added to a hot solution of sal-ammoniac, mixed with ammonia, a crystalline deposit is obtained on cooling the liquid, which is known as *fusible white precipitate*, and represents two molecules of hydrochlorate of ammonia, in which one-fourth of the hydrogen has been displaced by mercury, its composition being $N_2H_6Hg''Cl_2$. The same compound is formed when white precipitate is boiled with a solution of sal-ammoniac—



$$NH_2Hg''Cl + NH_3.HCl = N_2H_6Hg''Cl_2.$$

The above compounds possess a special interest for the chemist, as they were among the first to attract attention to the mobility of the hydrogen in ammonia, which has since been so well exemplified in the artificial production of organic bases by the action of ammonia upon the iodides of the alcohol-radicals. The relation of these compounds to each other is here exhibited:—

White precipitate,	$NH_2Hg''Cl$
Produced with corrosive sublimate in excess,	$(NH_2HgCl).HgCl_2$
,, by boiling with water,	$(NH_2HgCl).HgO$
,, ,, sal-ammoniac,	$N_2H_6Hg''Cl_2$
,, by heating to 600°	$(N_2Hg_3''.2HgCl_2)$

268. *Calomel*, *subchloride* or *protochloride of mercury*, or *mercurous chloride* (HgCl),* unlike corrosive sublimate, is insoluble in water, so that it is precipitated when hydrochloric acid or a soluble chloride is added to mercurous nitrate. The simplest mode of manufacturing it consists in intimately mixing one molecule of corrosive sublimate with 1 atom of metallic

* 2 vols. of vapour of calomel contain 2 vols. of mercury vapour and 1 vol. of chlorine. (See note on page 368.)

mercury, a little water being added to prevent dust, drying the mixture thoroughly, and subliming it; $HgCl_2 + Hg = 2HgCl$. But it is more commonly made by adding another atom of mercury to the materials employed in the preparation of corrosive sublimate. 2 parts by weight of mercury are dissolved, with the aid of heat, in 3 parts of oil of vitriol, and evaporated to dryness; $Hg + 2(H_2O.SO_3) = HgO.SO_3 + SO_2 + 2H_2O$. The residue of mercuric sulphate is intimately mixed with 2 more parts of mercury, and the mixture afterwards triturated with 1½ parts of common salt, until globules are no longer visible. The mixture is then heated, so that the calomel may pass off in vapour, which condenses as a translucent fibrous cake on the cool part of the subliming vessel, leaving sulphate of soda behind; $HgO.SO_3 + Hg + 2NaCl = 2HgCl + Na_2O.SO_3$. For medicinal purposes the calomel is obtained in a very fine state of division by conducting the vapour into a large chamber, so as to precipitate it in a fine powder by contact with a large volume of cold air. Steam is sometimes introduced to promote its fine division. Sublimed calomel always contains some corrosive sublimate, so that it must be thoroughly washed with water before being employed in medicine. When perfectly pure calomel is sublimed, a little is always decomposed during the process into metallic mercury and corrosive sublimate.

Calomel is met with either as a semitransparent fibrous mass, or an amorphous powder, with a slightly yellow tinge. It is heavier than corrosive sublimate (sp. gr. 7·18), and does not fuse before subliming; it may be obtained in four-sided prisms by slow sublimation. Diluted acids will not dissolve it, but boiling nitric acid gradually converts it into mercuric chloride and nitrate, which pass into solution. Alkaline solutions convert it into black suboxide of mercury, as is seen in *black-wash*, made by treating calomel with lime-water ($2HgCl + CaO = Hg_2O + CaCl_2$). Solution of ammonia converts it into a grey compound (NH_2Hg_2Cl), which is the analogue of white precipitate ($NH_2Hg''Cl$), containing Hg_2' in place of Hg''.

Mercurous iodide (HgI) is a green unstable substance, formed when iodine is triturated with an excess of mercury and a little alcohol. The beautiful scarlet *mercuric iodide* (HgI_2) has been noticed at p. 177. Its vapour has the remarkably high specific gravity 15·68.

If mercuric iodide be dissolved in iodide of potassium, the solution mixed with potash, and some ammonia added, a brown precipitate is formed, which may be represented by the formula $NHg''_2I.H_2O$; its formation can be explained by the equation, $2HgI_2 + 3KHO + NH_3 = NHg_2I.H_2O + 3KI + 2H_2O$.

A solution of mercuric iodide in iodide of potassium, mixed with potash, is employed as one of the most delicate tests (*Nessler's test*) for ammonia in waters; $\frac{1}{100}$ gr. of ammonia in half a pint of water is distinctly recognised by the brown yellow tinge caused by this test.

269. *Sulphides of mercury.*—When mercury is triturated with sulphur, the black *subsulphide of mercury* or *mercurous sulphide* (Hg_2S) is formed; it was termed by old writers *Ethiop's mineral*, and is an unstable compound easily resolvable into metallic mercury and *mercuric sulphide* (HgS). The latter has been mentioned as the principal ore of mercury, and is important as composing *vermilion.* The native sulphide of mercury, or *cinnabar*, is found sometimes in amorphous masses, sometimes crystallised in six-sided prisms varying in colour from dark brown to bright red. It may be distinguished from most other minerals by its great weight (sp. gr. 8·2), and by its red colour when scraped with a knife. Neither hydrochloric nor nitric acid, separately, will dissolve it, but a mixture of the two dis-

solves it as mercuric chloride, with separation of sulphur. Some specimens of cinnabar have a bright red colour, so that they only require grinding and levigating to be used as vermilion; and if the brown cinnabar in powder be heated for some time to 120° F. with a solution of sulphur in potash, it is converted into vermilion.

Of the artificial sulphide of mercury there are two varieties, the black, which is precipitated when corrosive sublimate is added to hydrosulphuric acid or a soluble sulphide, and the red (vermilion), into which the black variety is converted by sublimation, or by prolonged contact with solutions of alkaline sulphides containing excess of sulphur, though, so far as is known, the conversion is effected without chemical change, the red sulphide having the same composition as the black. In Idria and Holland, 6 parts of mercury and 1 of sulphur are well agitated together in revolving casks for several hours, and the black sulphide thus obtained is sublimed in tall earthern pots closed with iron plates, when the vermilion is deposited in the upper part of the pots, and is afterwards ground and levigated. The sublimed vermilion, however, is generally inferior to that obtained by the wet process, of which there are several modifications. One of the processes consists in triturating 300 parts of mercury with 114 parts of sulphur for two or three hours, and digesting the black product, at about 120° F., with 75 parts of hydrate of potash and 400 of water until it has acquired a fine red colour. The permanence of vermilion paint is, of course, attributable to the circumstance that it resists the action of light, of oxygen, carbonic acid, aqueous vapour, and even of the sulphuretted hydrogen and sulphurous or sulphuric acid which contaminate the air of towns, whereas the red paints containing lead are blackened by sulphuretted hydrogen, and all vegetable and animal reds are liable to be bleached by atmospheric oxygen and by sulphurous acid.

When the black precipitated mercuric sulphide is boiled with solution of corrosive sublimate, it is converted into a white *chlorosulphide of mercury*, $HgCl_2.2HgS$, which is also formed when a small quantity of hydrosulphuric acid is added to corrosive sublimate.

It is remarkable that the molecule of vermilion, HgS, occupies 3 vols. instead of 2, containing 2 vols. of mercury vapour combined with 1 vol. of sulphur vapour. The anomaly might be explained on the supposition that the high temperature requisite to convert the vermilion into vapour suffices to suspend the attraction between its elements, so that the vapour of which the specific gravity is taken is not really that of the compound of mercury and sulphur (which should occupy 2 vols.), but a *mixture* of the 2 vols. of mercury vapour and 1 vol. of sulphur vapour, occupying 3 vols. This view of the temporary decomposition of the vapour receives some slight support from the convertibility of the black into the red sulphide by sublimation.

BISMUTH.

Bi''' = 210 parts by weight.

270. Bismuth, though useful in various forms of combination, is too brittle to be employed in the pure metallic state. It is readily distinguished from other metals by its peculiar reddish lustre and its highly crystalline structure, which is very perceptible upon a freshly broken surface; large cubical (or, strictly speaking, rhombohedral) crystals of bismuth are easily obtained by melting a few ounces in a crucible, allow-

ing it to cool till a crust has formed upon the surface, and pouring out the portion which has not yet solidified, when the crystals are found lining the interior of the crucible. It is somewhat lighter than lead (sp. gr. 9·8), and volatilises more readily at high temperatures.

Unlike most other metals, bismuth is found chiefly in the metallic state, disseminated, in veins, through gneiss and clay-slate. The chief supply is derived from the mines of Schneeberg, in Saxony, where it is associated with the ores of cobalt.

In order to extract the metal from the masses of earthy matter through which it is distributed, advantage is taken of its very low fusing point (507° F.) The ore is broken into small pieces, and introduced into iron cylinders which are fixed in an inclined position over a furnace (fig. 271). The upper opening of the cylinders, through which the ore is introduced, is provided with an iron door, and the lower opening is closed with a plate of fire-brick perforated for the escape of the metal, which flows out when the cylinders are heated, into iron receiving pots, which are kept hot by a charcoal fire.

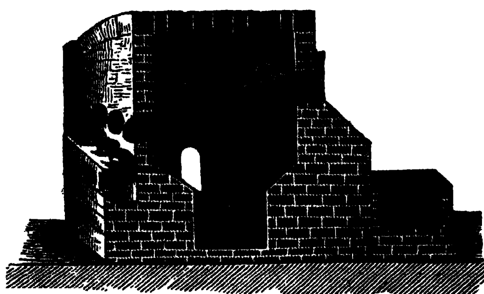


Fig. 271.—Extraction of bismuth.

Commercial bismuth generally contains considerable quantities of arsenic, sulphur, and silver; it is sometimes *cupelled* in the same manner as lead, in order to extract the silver, the oxide of bismuth being afterwards again reduced to the metallic state by heating it with charcoal. Pure bismuth dissolves entirely and easily in diluted nitric acid (sp. gr. 1·2); but if it contains arsenic, a white deposit of arseniate of bismuth is obtained. Hydrochloric and diluted sulphuric acids will not act upon bismuth.

The chief use of bismuth is in the preparation of certain alloys with other metals. Some kinds of type metal and stereotype metal contain bismuth, which confers upon them the property of expanding in the mould during solidification, so that they are forced into the finest lines of the impression.

This metal is also remarkable for its tendency to lower the fusing point of alloys, which cannot be accounted for merely by referring to the low fusing point of the metal itself. Thus, an alloy of 2 parts bismuth, 1 part lead, and 1 part tin, fuses below the temperature of boiling water, although the most fusible of the three metals, tin, requires a temperature of 442° F. An alloy of this kind is used for soldering pewter. Bismuth is also employed, together with antimony, in the construction of thermo-electric piles.

271. *Oxides of bismuth.*—Three compounds of bismuth with oxygen have been prepared; bismuthous oxide BiO, bismuthic oxide Bi_2O_3, and bismuthic acid Bi_2O_5.

Bismuthous oxide (BiO) is obtained as a black precipitate by reducing terchloride of bismuth with protochloride of tin in the presence of an excess of potash. It is easily converted into bismuthic oxide when heated in contact with air.

Bismuthic oxide (Bi_2O_3), is the basic and most important oxide of the metal. It is formed when bismuth is heated in air, or when nitrate of bismuth is decomposed

by heat, and is a yellow powder which becomes brown when heated, and fuses easily. Bismuthic oxide forms the rare mineral *bismuth-ochre.*

Bismuthic acid (Bi_2O_5) is formed when bismuthic oxide is suspended in a strong solution of potash through which chlorine is passed, when a red solution of bismuthate of potash is obtained, and hydrated bismuthic acid ($H_2O.Bi_2O_5$) is precipitated as a red powder, which becomes brown and anhydrous at 270° F. It is easily decomposed by heat, evolving oxygen and leaving $Bi_2O_3.Bi_2O_5$. When heated with acids it also evolves oxygen, and forms salts of bismuthic oxide. The bismuthates of the alkalies are very unstable, being decomposed by water.

272. The only two salts of bismuth which are known in the arts are the *basic nitrate* (*trisnitrate of bismuth* or flake-white) and the *oxychloride of bismuth* (*pearl-white*). The preparation of these compounds illustrates one of the characteristic properties of the salts of bismuth, viz., the facility with which they are decomposed by water with the production of insoluble basic salts.

If bismuth be dissolved in nitric acid, it acquires oxygen from the latter, and becomes sesquioxide of bismuth, which combines with nitric acid to form the nitrate of bismuth ($Bi_2O_3.3N_2O_5$), and this may be obtained in prismatic crystals of the composition $Bi_2O_3.3N_2O_5.10Aq$. If the solution be mixed with a large quantity of water, it deposits a precipitate of *flake-white* ($Bi_2O_3.N_2O_5.H_2O$), or basic nitrate of bismuth, the remainder of the nitric acid being left in the solution.

Pearl-white has the composition $2(BiCl_3.Bi_2O_3).H_2O$, and is obtained by dissolving bismuth in nitric acid, and pouring the solution into water in which common salt has been dissolved.

Terchloride of bismuth ($BiCl_3$) may be distilled over when bismuth is heated in a current of dry chlorine; it is a deliquescent fusible solid, easily dissolved by hydrochloric acid, but decomposed by water, with formation of the above-mentioned *oxychloride of bismuth;* $3BiCl_3 + 3H_2O = BiCl_3.Bi_2O_3 + 6HCl$. This compound is so insoluble in water that nearly every trace of bismuth may be precipitated from a moderately acid solution of the terchloride by adding much water.

Bismuthous sulphide (BiS) is sometimes found in nature, but more frequently *bismuthic sulphide* (Bi_2S_3) or *bismuth glance,* which occurs in dark-grey lustrous prisms isomorphous with native sulphide of antimony. It is also obtained as a black precipitate by the action of hydrosulphuric acid upon bismuthic salts. Bismuthic sulphide is not soluble in diluted sulphuric or hydrochloric acid, but dissolves easily in nitric acid.

ANTIMONY.

$Sb''' = 122$ parts by weight.

273. Antimony is nearly allied to bismuth in both its physical and chemical characters. It is even harder and more brittle than that metal, being easily reduced to a black powder. Its highly crystalline structure is another very well-marked feature, and is at once perceived upon the surface of an ingot of antimony, where it is exhibited in beautiful fern-like markings (*star antimony*). Its crystals belong to the same system (the rhombohedral) as those of bismuth and arsenic. It is much lighter than bismuth (sp. gr. 6·715), and requires a higher temperature (800° F.) to fuse it, though it is more easily converted into vapour, so that, when strongly heated in air, it emits a thick white smoke, the vapour being oxidised. Like bismuth, it is but little affected by hydrochloric or dilute sulphuric acid, but nitric acid oxidises it, though it dissolves very little of the metal, the greater part being left in the form of antimonic acid. The best mode of dissolving antimony is to boil it with hydrochloric acid and to add nitric acid by degrees.

Antimony is chiefly found in nature as *grey antimony ore* or sulphide

of antimony (Sb_2S_3), which occurs in Cornwall, but much more abundantly in Hungary. It is found in veins associated with galena, iron pyrites, quartz, and heavy spar. In order to purify it from these, advantage is taken of its easy fusibility, the ore being heated upon the hearth of a reverberatory furnace, with some charcoal to prevent oxidation, when the sulphide of antimony melts and collects below the impurities, whence it is run off and cast into moulds. The product thus obtained is known in commerce as *crude antimony*, and contains sulphides of arsenic, iron, and lead.

To obtain *regulus of antimony* or metallic antimony, the sulphide of antimony is sometimes fused in contact with refuse metallic iron (such as the clippings of tin-plate), when sulphide of iron is formed, and collects as a fused slag upon the surface of the melted antimony—



$$Sb_2S_3 + Fe_3 = 3FeS + Sb_2.$$

The antimony thus obtained always contains a considerable proportion of iron.

A purer product is procured by another process, which consists in roasting the sulphide in a reverberatory furnace at a temperature insufficient to fuse it, for about twelve hours, when most of the sulphur and arsenic are expelled as sulphurous and arsenious acids, carrying with them a considerable quantity of oxide of antimony. The roasted ore has a brown-red colour, and contains both oxide and sulphide of antimony: it is mixed into a paste with $\frac{1}{8}$ its weight of charcoal saturated with a strong solution of carbonate of soda. The mixture is strongly heated in crucibles, when the oxide of antimony is reduced by the charcoal, and a portion of the sulphide, having been converted into oxide by double decomposition with the soda ($Sb_2S_3 + 3Na_2O = Sb_2O_3 + 3Na_2S$), is also reduced, the remainder of the sulphide combining with the sulphide of sodium to form a slag which floats above the metallic antimony; the latter is cast into ingots for the market, and the slag, known as *crocus of antimony* (chiefly $3Na_2S.Sb_2S_3$), is employed for the preparation of some of the compounds of the metal.

On the small scale, antimony may be extracted from the sulphide by fusing it in an earthen crucible with 4 parts of commercial cyanide of potassium, at a moderate heat; or by mixing 4 parts of the sulphide with 3 of bitartrate of potash and $1\frac{1}{2}$ of nitre, and throwing the mixture, by small portions, into a red-hot crucible, when the sulphur is oxidised, and converted into sulphate of potash, by the nitre, which is not present in sufficient quantity to oxidise the antimony, so that the metal collects at the bottom of the crucible.

The brittleness of antimony renders it useless in the metallic state except for the construction of thermo-electric piles, where it is employed in conjunction with bismuth. Antimony is employed, however, to harden several useful alloys, such as type-metal, shrapnel-shell bullets, Britannia metal, and pewter.

Amorphous antimony.—The ordinary crystalline form of antimony may be obtained, like copper and other metals, by decomposing solutions containing the metal by transmitting the galvanic current; but in some cases the antimony is deposited from very strong solutions in an amorphous condition, having properties very different from those of ordinary antimony. The best mode of obtaining it in this form is to decompose a solution of 1 part of tartar emetic (tartrate of antimony and potash) in 4 parts of a strong solution of terchloride of antimony (obtained by heating hydrochloric acid with sulphide of antimony till it refuses to dissolve any more), by the aid of three cells of Smee's battery, the zinc of which is connected by a copper wire with a plate of copper immersed in the antimonial solution, whilst the platinised silver of the battery is connected with a plate of antimony in the same solution, at

some little distance from the copper plate. The deposit of antimony which forms upon the copper has a brilliant metallic appearance, but is amorphous, and not crystalline, like the ordinary metal. If it be gently heated or sharply struck, its temperature suddenly rises to about 400°, and it becomes converted into a form more nearly resembling crystalline antimony. At the same time, however, thick fumes of terchloride of antimony are evolved, for this substance is always present in the amorphous antimony to the amount of 5 or 6 per cent.,* so that, as yet, there is not sufficient evidence to establish beyond a doubt the existence of a pure amorphous form of antimony corresponding to amorphous phosphorus, however probable this may appear from the chemical resemblance between these elements.

274. *Oxides of antimony.*—There are two well-known oxides of antimony, the sesquioxide (Sb_2O_3) and antimonic acid (Sb_2O_5). *Teroxide* or *sesquioxide of antimony*, or *antimonic oxide*, is formed when antimony burns in air, and is prepared on a large scale by roasting either the metal or the sulphide in air, for use in painting as a substitute for white lead. It is also found in nature as *white antimony ore* or *valentinite*. Antimonic oxide forms a crystalline powder usually composed of minute prisms having the shape of the rarer form of arsenious acid (p. 250), whilst occasionally it is obtained in crystals similar to those of the common octahedral arsenious acid, with which, therefore, antimonic oxide is *isodimorphous.*† When heated in air it assumes a yellow colour, afterwards takes fire, smoulders, and becomes converted into the antimoniate of teroxide of antimony ($Sb_2O_3.Sb_2O_5 = Sb_2O_4$), which was formerly regarded as an independent oxide. The teroxide is insoluble in water, but acids dissolve it, forming salts, though its basic properties are weak, and its salts rather ill defined. Potash and soda are also capable of dissolving it, whence it is sometimes called *antimonious acid.*‡

Antimonic acid (Sb_2O_5) is formed when antimony is oxidised with nitric acid; it then forms a white powder, which should be well washed and dried. When heated it becomes pale yellow, and is decomposed at a high temperature, leaving $Sb_2O_3.Sb_2O_5$. It is dissolved by solution of potash forming antimoniate of potash.

A better method of obtaining the antimoniate of potash consists in gradually adding 1 part of powdered antimony to 4 parts of nitre fused in a clay crucible, when the oxygen of the nitre converts the antimony into antimonic acid, which combines with the potash. The mass is powdered and washed with warm water to remove the excess of nitre and the nitrate of potash, when the insoluble anhydrous antimoniate of potash is left; and on boiling this for an hour or two with water, it becomes hydrated and dissolves. The solution, when evaporated, leaves a gummy mass of *antimoniate of potash*, having the composition $K_2O.Sb_2O_5.5Aq$.

When the solution of antimoniate of potash is treated with carbonic acid, a crystalline precipitate of biantimoniate of potash ($K_2O.2Sb_2O_5$) is obtained. If antimoniate of potash be fused (in a silver crucible) with hydrate of potash, it becomes converted into *metantimoniate of potash* ($2K_2O.Sb_2O_5$), which is decomposed by water into potash and *bimetantimoniate of potash* ($K_2O.H_2O.Sb_2O_5$), which may be crystallised from the solution. This latter salt is valuable as a test for soda, since the bimetan-

* It has been plausibly suggested that the sudden rise of temperature may be due to the presence of an antimony compound analogous to the so-called chloride of nitrogen, the latter element being connected with antimony by several chemical analogies.

† The octahedral form appears to be produced only when the prismatic form is slowly sublimed in a non-oxidising atmosphere. The mineral *exitèle* is prismatic oxide of antimony, and *senarmontite* is the octahedral form of that oxide.

‡ Two crystallised *antimonites of soda* have been obtained, the neutral antimonite $Na_2O.Sb_2O_3.6Aq.$, and the terantimonite $Na_2O.3Sb_2O_3.2Aq.$; the former is sparingly soluble, the latter almost insoluble in water.

timoniate of soda, $Na_2O.H_2O.Sb_2O_5$, is one of the very few salts of soda which are insoluble in water, and is therefore obtained as a crystalline precipitate when the bimetantimoniate of potash is added to a solution containing soda. The solution of bimetantimoniate of potash is gradually changed by keeping, into antimoniate of potash ($K_2O.Sb_2O_5$), which does not so readily precipitate soda.

It will be remarked that the antimoniates correspond in composition with the monobasic (or meta) phosphates, whilst the metantimoniates represent the bibasic (or pyro) phosphates.

Naples yellow is a compound of antimonic acid with oxide of lead.

275. *Antimonietted hydrogen* (SbH_3?) is obtained, mixed with free hydrogen, when an alloy of zinc and antimony is acted on by diluted sulphuric acid, or when a solution of a salt of antimony (tartar emetic, for example) is poured into a hydrogen apparatus containing zinc and dilute sulphuric acid (fig. 272). If the gas be inflamed as it issues into the air, it burns with a livid flame, emitting fumes of antimonic oxide, and when a piece of glass or porcelain is depressed in the flame (fig. 273) it becomes coated with a black film of metallic antimony. A red heat decomposes the gas into its elements, so that if the tube through which it is passing be heated with a spirit lamp (fig. 274) a lustrous black deposit of antimony will be formed just beyond the heated part. The composition of antimonietted hydrogen is not certainly established, since it has never been obtained unmixed with hydrogen; but it is believed to contain SbH_3, because, when passed into nitrate of silver, it gives a black precipitate containing $SbAg_3$. It would then be analogous to ammonia (NH_3), phosphuretted hydrogen (PH_3), and arsenietted hydrogen (AsH_3). Very minute quantities of antimony are detected in chemical analysis by converting it into this form.

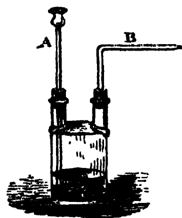


Fig. 272.

Fig. 273.

276. CHLORIDES OF ANTIMONY.—Chlorine and antimony combine readily, with evolution of heat and light; the chlorides are among the most important compounds of this metal.

Terchloride of antimony ($SbCl_3$) may be prepared by distilling 3 parts of powdered antimony with 8 parts of corrosive sublimate, when calomel and an amalgam of antimony are left, and the terchloride of antimony (boiling at 433° F.) distils over—



$$Sb_2 + 2HgCl_2 = SbCl_3 + SbHg + HgCl.$$

It can also be obtained by boiling powdered antimony or sulphide of antimony to dryness with strong sulphuric acid, and distilling the sulphate of teroxide of antimony thus obtained, with common salt. The terchloride is a soft grey crystalline fusible solid, whence its old name of *butter of antimony*. It may be dissolved in a small quantity of water, but a large quantity of water decomposes it, forming a bulky white precipitate, which is an

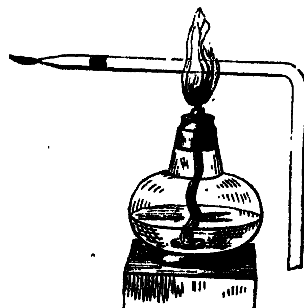
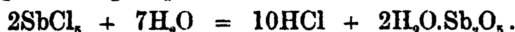


Fig. 274.

oxychloride of antimony ($3SbCl_3 + 3H_2O = SbCl_3.Sb_2O_3 + 6HCl$). When hot water is added to a hot solution of terchloride of antimony in hydrochloric acid, minute prismatic needles are deposited, containing $2SbCl_3.5Sb_2O_3$, and formerly called *powder of Algaroth.* The terchloride of antimony, in its behaviour with water, much resembles that of bismuth. Terchloride of antimony is occasionally used in surgery as a caustic; it also serves as a bronze for gun-barrels, upon which it deposits a film of antimony.

Pentachloride of antimony ($SbCl_5$) is prepared by heating coarsely powdered antimony in a retort, through which a stream of dry chlorine is passed (fig. 216), the neck of the retort being fitted into an adapter, which serves to condense the pentachloride. One ounce of antimony will require the chlorine from about 6 oz. of common manganese and 18 oz. (measured) of hydrochloric acid. The pure pentachloride is a colourless fuming liquid of a very suffocating odour; it combines energetically with a small quantity of water, forming a crystalline hydrate, but an excess of water decomposes it into hydrochloric and hydrated metantimonic acids, the latter forming a white precipitate—



$$2SbCl_5 + 7H_2O = 10HCl + 2H_2O.Sb_2O_5.$$

Pentachloride of antimony is employed by the chemist as a chlorinating agent; thus, olefiant gas (C_2H_4) when passed through it, is converted into Dutch liquid ($C_2H_4Cl_2$), and carbonic oxide into phosgene gas, the pentachloride of antimony being converted into terchloride.

The pentachloride of antimony is the analogue of pentachloride of phosphorus, and a *chlorosulphide of antimony* ($SbCl_3S$), corresponding to chlorosulphide of phosphorus, is obtained as a white crystalline solid by the action of hydrosulphuric acid upon pentachloride of antimony.

277. *Sulphides of antimony.*—The *tersulphide* or *sesquisulphide* of antimony (Sb_2S_3) has been noticed as the chief ore of antimony. It is a heavy mineral (sp. gr. 4·63) of a dark-grey colour and metallic lustre, occurring in masses which are made up of long prismatic needles. It fuses easily, and may be sublimed unchanged out of contact with air. It is easily recognised by heating it, in powder, with hydrochloric acid, when it evolves the odour of hydrosulphuric acid, and if the solution be poured into water, it deposits an orange precipitate. This orange sulphide, which has the same composition as the grey sulphide, is also obtained by adding hydrosulphuric acid to a solution of a salt of antimony (for example, tartar-emetic) acidulated with hydrochloric acid. It may be converted into the grey sulphide by the action of heat. The orange variety constitutes the *antimony vermilion*, the preparation of which has been described at p. 214. Native tersulphide of antimony is employed, in conjunction with chlorate of potash, in the *friction-tube* for firing cannon; it is also used in *percussion caps*, together with chlorate of potash and fulminate of mercury. Its property of deflagrating with a bluish-white flame when heated with nitre, renders it useful in compositions for coloured fires.

Glass of antimony is a transparent red mass obtained by roasting the tersulphide of antimony in air, and fusing the product; it contains about 8 parts of teroxide and 1 part of tersulphide of antimony.

Red antimony ore is an oxysulphide of antimony, $Sb_2O_3.2Sb_2S_3$.

Pentasulphide of antimony (Sb_2S_5) is obtained as a bright orange-red precipitate by the action of hydrosulphuric acid upon a solution of pentachloride of antimony in hydrochloric acid.

Both the sulphides of antimony are sulphur-acids, capable of combining with the alkaline sulphides to form *sulphantimonites* and *sulphantimoniates* respectively. Hence they are easily dissolved by alkalies and alkaline sulphides. Even metallic antimony, in powder, is dissolved when gently heated with solution of sulphide of potassium in which sulphur has been dissolved, any lead or iron which may be present being left in the residue, so that the antimony may be tested by this process as to its freedom from those metals.

Mineral kermes is a variable mixture of sesquioxide and sesquisulphide of antimony, which is deposited as a reddish-brown powder from the solution obtained by boiling sesquisulphide of antimony with potash or soda. It was formerly much valued for medicinal purposes.

Schlippe's salt is the sulphantimoniate of sulphide of sodium ($3Na_2S, Sb_2S_5, 18H_2O$) and may be obtained in fine transparent tetrahedral crystals.

TIN.

Sn = 118 parts by weight.

278. Tin is by no means so widely diffused as most of the other metals which are largely used, and is scarcely ever found in the metallic state in nature. Its only important ore is that known as *tin-stone*, which is a binoxide of tin (SnO_2), and is generally found in veins traversing quartz, granite, or slate. It is generally associated with arsenical iron pyrites, and with a mineral called *wolfram*, which is a compound of tungstic acid (WO_3) with the oxides of iron and manganese.

Tin-stone is sometimes found in alluvial soils in the form of detached rounded masses; it is then called *stream tin ore*, and is much purer than that found in veins, for it has undergone a natural process of oxidation and levigation exactly similar to the artificial treatment of the impure ore. These detached masses of stream tin ore are not unfrequently rectangular prisms with pyramidal terminations.

The Cornish mines furnish the largest supplies of tin, and those of Malacca and Banca stand next. Tin-stone is also found in Bohemia, Saxony, and California. At the Cornish tin-works the purer portions of the ore are picked out by hand, and the residue, which contains quartz and other earthy impurities, together with copper pyrites and arsenical iron pyrites, is reduced to a coarse powder in the stamping-mills, and washed in a stream of water. The tin-stone, being extremely hard, is not reduced to so fine a powder as the pyritous minerals associated with it, and these latter are therefore more readily carried away by the stream of water than the tin-stone. The removal of the foreign matters from the ore is also much favoured by the high specific gravity of the binoxide of tin, which is 6·5, whilst that of sand or quartz is only 2·7, so that the latter would be carried off by a stream which would not disturb the former. So easily and completely can this separation be effected, that a sand containing less than one per cent. of tin-stone is found capable of being economically treated.

In order to expel any arsenic and sulphur which may still remain in the washed ore, it is roasted in quantities of 8 or 10 cwts. in a reverberatory furnace, when the sulphur is disengaged in the form of sulphurous acid, and the arsenic in that of arsenious acid, the iron being left in the state of sesquioxide, and the copper partly as sulphate of copper, partly

as unaltered sulphide. To complete the oxidation of the insoluble sulphide of copper, and its conversion into the soluble sulphate, the roasted ore is moistened with water and exposed to the air for some days, after which the whole of the copper may be removed by again washing with water.

A second washing in a stream of water also removes the sesquioxide of iron in a state of suspension, and this is much more easily effected than when the iron was in the form of pyrites, since the difference between the specific gravity of this mineral (5·0) and that of the tin-stone (6·5) is far less than that between sesquioxide of iron and tin-stone.

The ore thus purified contains between 60 and 70 per cent. of tin; it is mixed very intimately with about ⅛ of powdered coal, and a little lime or fluor spar to form a fusible slag with the earthy impurities; the mixture is sprinkled with water to prevent its dispersion by the draught of air, and thrown on the hearth (A, fig. 275) of a reverberatory furnace, in charges of between 20 and 25 cwts.

The temperature is not permitted to rise too high at first, lest a portion of the oxide of tin should combine with the silicic acid to form a silicate, from which the metal would be reduced with difficulty.



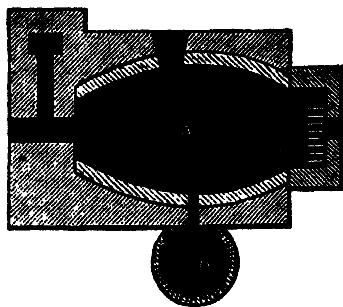


Fig. 275.

During the first 6 or 8 hours the doors of the furnace are kept shut, so as to exclude the air and favour the reducing action of the carbon upon the binoxide of tin, the oxygen of which it converts into carbonic oxide, leaving the tin in the metallic state to accumulate upon the hearth beneath the layer of slag. When the reduction is deemed complete, the mass is well stirred with an iron paddle to separate the metal from the slag; the latter is run out first, and the tin is then drawn off into an iron pan (B), where it is allowed to remain at rest for the dross to rise to the surface, and is ladled out into ingot-moulds.

The slags drawn out of the smelting-furnace are carefully sorted, those which contain much oxide of tin being worked up with the next charge of ore, whilst those in which globules of metallic tin are disseminated are crushed, so that the metal may be separated by washing in a stream of water.

The tin, when first extracted from the ore, is far from pure, being contaminated with small quantities of iron, arsenic, copper, and tungsten. In order to purify it from these, the ingots are piled into a hollow heap near the fire-bridge of a reverberatory furnace, and gradually heated to the fusing point, when the greater portion of the tin flows into an outer basin, whilst the remainder is converted into the binoxide, which remains as dross upon the hearth, together with the oxides of iron, copper, and tungsten, the arsenic having passed off in the form of arsenious acid. Fresh ingots of tin are introduced at intervals, until about 5 tons of the metal have collected in the basin, which is commonly the case in about an hour after the commencement of the operation.

The specific gravity of tin being very low (7·285), any dross which may still remain mingled with it does not separate very readily; to obviate this, the molten metal is well agitated by stirring with wet wooden poles, or lowering billets of wet wood into it, when the evolved bubbles of steam carry the impurities up to the surface in a kind of froth; the stirring is continued for about three hours, and the metal is allowed to remain at rest for two hours, when it is skimmed and ladled into ingot-moulds. It is found that, in consequence of the lightness of the metal, and its tendency to separate from the other metals with which it is contaminated, the ingots which are cast from the metal first ladled out of the pot are purer than those from the bottom; this is shown by striking the hot ingots with a hammer, when they break up into the irregular prismatic fragments known as *dropped* or *grain-tin*, the impure metal not exhibiting this extreme brittleness at a high temperature. The tin imported from Banca is celebrated for its purity (*Straits tin*).

When the tin ore contains wolfram, it is usual to purify it before smelting, by fusion with carbonate of soda in a reverberatory furnace, when the tungstic acid is converted into tungstate of soda, which is dissolved out by water and crystallised. This salt finds an application in calico-printing.

On the small scale, tin may be extracted from tin-stone, by fusing 100 grains with 20 grains of dried carbonate of soda, and 20 of dried borax, in a crucible lined with charcoal, exactly as in the extraction of iron (see p. 319).

279. By its physical characters, tin is very readily distinguished from other metals. If a bar of tin be bent, it emits a peculiar crackling sound. With the exception of lead and zinc, it is the least tenacious of all the metals in common use; its ductility is therefore very low, and lead is the only common metal which is more difficult to draw into wire at the ordinary temperature. Tin may, however, be drawn at 212° F.

In fusibility, tin surpasses all the other common metals, becoming liquid at 442° F., but it is not easily vaporised. Its malleability is also very great, only gold, silver, and copper exhibiting this quality in a higher degree. This malleability is shown in the manufacture of *tin-foil*, where plates of the best tin are hammered down to a certain thinness, then cut up, laid upon each other, and again beaten till extended to the required degree.

Tin-plate, it must be remembered, is made in a very different way, by coating sheets of iron with a layer of tin; the best kind, known as *block tin*, being that which is covered with the thickest layer of tin, and afterwards hammered upon a polished anvil in order to consolidate the coating and make it adhere more firmly. Tin, being unaltered by exposure to air at the ordinary temperature, will effectually protect the iron from rust as long as the coating of tin is perfect, but as soon as a portion of the tin is removed so as to leave the iron exposed, corrosion will take place very rapidly, because the two metals form a galvanic couple, which will decompose the water (charged with carbonic acid) deposited upon them from the air, and the iron having the greater attraction for oxygen, will be the metal attacked. In the case of galvanised iron (coated with zinc), on the contrary, the zinc would be the metal attacked, and hence the greater durability of this material under certain conditions.

For the manufacture of tin-plate, the very best iron refined with char-

coal (see p. 308) is employed, and the most important part of the process consists in cleansing the iron plates from every trace of oxide which would prevent the adhesion of the tin. To effect this they are made to undergo several processes, of which the most important are—(1), immersion in diluted sulphuric acid; (2), heating to redness; (3), hammering and rolling to scale off the oxide; (4), steeping in sour bran; (5), immersion in mixed diluted sulphuric and hydrochloric acids; (6), scouring with bran; (7), washing with water; they are then dried for an hour in a vessel of melted tallow which prevents contact of air, and immersed for an hour and a half in melted tin, the surface of which is protected from oxidation by tallow; after draining, they are dipped a second time into the tin to thicken the layer; then transferred to a bath of hot tallow to allow the superfluous tin to run down to the lower edge, whence it is afterwards removed by liquefying it in a vessel of melted tin, and shaking it off by a sharp blow. About 8 lbs. of tin are required to cover 225 plates, weighing 112 lbs.

Terne-plate is iron coated with an alloy of tin and lead.

In tinning the interior of copper vessels, in order to prevent the contamination of food with the copper, the surface is first thoroughly cleaned from oxide by heating it and rubbing over it a little sal-ammoniac (hydrochlorate of ammonia, $NH_3.HCl$), which decomposes any oxide of copper, converting it into the volatile chloride of copper ($CuO + 2(NH_3.HCl) = CuCl_2 + H_2O + 2NH_3$). A little resin is then sprinkled upon the metallic surface, to protect it from oxidation, and the melted tin is spread over it with tow.

Pins (made of brass wire) are coated with tin by boiling them with cream of tartar (bitartrate of potash), common salt, alum, granulated tin, and water; the tin is oxidised at the expense of the water, and is then dissolved by the acid liquid, from which solution it is reduced by electrolytic action, for the tin is more highly electro-positive than the brass, and the latter acts as the negative plate.

280. *Alloys of tin.*—The solder employed for tin wares is an alloy of tin and lead in various proportions, sometimes containing 2 parts of tin to 1 of lead (fine solder), sometimes equal weights of the two metals (common solder), and sometimes 2 parts of lead to 1 of tin (coarse solder). All these alloys melt at a lower temperature than tin, and, therefore, than lead. In applying solder, it is essential that the surfaces to be united be quite free from oxide, which would prevent the adhesion of the solder; this is insured by the application of sal-ammoniac, or of hydrochloric acid,* or sometimes of powdered borax, remarkable for its ready fusibility and its solvent power for the metallic oxides.

Tin forms the chief part of the alloys known as pewter and Britannia metal, the former being composed of about 4 parts of tin and 1 of lead, whilst the latter contains, in addition to the tin, comparatively small quantities of antimony, copper, and lead. Another similar alloy is composed of 12 parts of tin, 1 of antimony, and a little copper.

Gun metal is an alloy of 90·5 parts of copper with 9·5 of tin, especially valuable for its tenacity, hardness, and fusibility. In preparing this alloy, it is usual to melt the tin, in the first place, with twice its weight of copper, when a white, hard, and extremely brittle alloy (*hard metal*) is

* It is customary to *kill* the hydrochloric acid by dissolving some zinc in it. The chloride of zinc is probably useful in protecting the work from oxidation.

obtained. The remainder of the copper is fused in a deoxidising flame on the hearth of a reverberatory furnace, and the hard metal thoroughly mixed with it, long wooden stirrers being employed. A quantity of old gun metal is usually melted with the copper, and facilitates the mixing of the metals. When the metals are thoroughly mixed, the oxide is removed from the surface, and the gun metal is run into moulds made of loam, the stirring being continued during the running, in order to prevent the separation, to which this alloy is very liable, of a white alloy containing a larger proportion of tin, which has a lower specific gravity, and would chiefly collect in the upper part of the casting. In casting cannon (erroneously called *brass* guns), the mould is placed perpendicularly with the muzzle upwards, the upper part of the mould being about 3 feet longer than is required for the gun, so that a superfluous cylinder of metal or *dead-head* is formed, in which the separated alloy collects, together with any oxide or dross which may have run out with the metal; probably, also, the weight of this column of metal hastens the solidification and hinders the separation of the metals, at the same time increasing the density and consequent tenacity of the metal at the breech of the gun; this dead-head is cut off before the gun is turned and bored. The metal is run into the mould at a temperature as near its point of solidification as possible, so as to diminish the chance of separation. The purest commercial qualities of copper and tin are always employed in gun metal.

Bronze is essentially an alloy of copper and tin, containing more tin than gun metal; its composition is varied according to its application, small quantities of zinc and lead being often added to it. Bronze is affected by changes of temperature, in a manner precisely the reverse of that in which steel is influenced, for it becomes hard and brittle when allowed to cool slowly, but soft and malleable when quickly cooled. The art of making bronze was practised before any progress had been made in working iron, and ancient weapons were very commonly of this material.

Bronze coin (substituted for the copper coinage) is composed of 95 copper, 4 tin, and 1 zinc.

Bell metal is an alloy of about 4 parts of copper and 1 of tin, to which lead and zinc are sometimes added. The metal of which musical instruments are made generally contains the same proportions of copper and tin as bell metal.

Speculum metal, employed for reflectors in optical instruments, consists of 2 parts of copper and 1 of tin, to which a little zinc, arsenic, and silver are sometimes added to harden it and render it susceptible of a high polish.

A superior kind of *type metal* is composed of 1 part of tin, 1 of antimony, and 2 of lead.

Tin is not dissolved by nitric acid, but is converted into a white powder, the binoxide of tin; hydrochloric acid dissolves it with the aid of heat, evolving hydrogen; but the best solvent for tin is a mixture of hydrochloric with a little nitric acid. When the metal is acted upon by hydrochloric acid, it assumes a crystalline appearance, which has been turned to account for ornamenting tin-plate. If a piece of common tin-plate be rubbed over with tow dipped in a warm mixture of hydrochloric and nitric acids, its surface is very prettily diversified (*moiré métallique*); it is usual to cover the surface with a coloured transparent varnish.

Commercial tin is liable to contain minute quantities of lead, iron, copper, arsenic, antimony, bismuth, gold, molybdenum, and tungsten. Pure tin may be precipitated in crystals by the feeble galvanic current excited by immersing a plate of tin in a strong solution of stannous chloride, covered with a layer of water, so that the metal may be in contact with both layers of liquid.

281. Oxides of Tin.—Two oxides of this metal are known—the protoxide, SnO, and the binoxide, SnO_2.

Protoxide of tin (SnO), or *stannous oxide*, is a substance of little practical importance, obtained by decomposing stannous chloride with an alkali. Its colour varies, according to the mode of preparing it, from black or olive-coloured to red. It is a feebly basic oxide, and therefore dissolves in the acids; it may also be dissolved by a strong solution of potash, but is then easily decomposed into metallic tin and the binoxide which combines with the potash.

Binoxide of tin (SnO_2) or *stannic oxide*, has been mentioned as the chief ore of tin, and is formed when tin is heated in air. *Tin-stone*, or *cassiterite*, as the natural form of this oxide is called, occurs in very hard, square prisms, usually coloured brown by peroxide of iron. In its insolubility in acids it resembles crystallised silica, and, like that substance, it forms, when fused with alkalies or their carbonates, compounds which are soluble in water; these compounds are termed *stannates*, the binoxide of tin being known as *stannic acid*.

Stannate of soda is prepared, on the large scale, for use as a mordant by calico-printers. The prepared tin ore (p. 379) is heated with solution of hydrate of soda, and boiled down till the temperature rises to 500° or 600° F.; or the tin ore is fused with nitrate of soda, when the nitric acid is expelled. It crystallises easily in hexagonal tables having the composition $Na_2O.SnO_2$, 4Aq., which dissolve easily in cold water, and are partly deposited again when the solution is heated. Most neutral salts of the alkalies also cause a separation of stannate of soda from its aqueous solution. The solution of stannate of soda has, like the silicate, a strong alkaline reaction, and when neutralised by an acid, yields a precipitate of hydrated stannic acid, $H_2O.SnO_2$. If the solution of stannate of soda be added to an excess of hydrochloric acid, the stannic acid remains in solution, and if the liquid be dialysed (see p. 111), a jelly is first formed, which gradually liquefies as the chloride of sodium diffuses away, and eventually a pure aqueous solution of stannic acid is obtained, which is very easily gelatinised by the addition of a minute quantity of hydrochloric acid, or of some neutral salt. The great similarity between stannic and silicic acids is here very remarkable. When heated, stannic acid is converted into metastannic acid.

Metastannic acid (Sn_5O_{10}) is obtained as a white crystalline hydrate when tin is oxidised by nitric acid; when washed with water and dried by exposure to air, it has the composition $Sn_5O_{10}.10H_2O$, but when dried at 212° F. it becomes $Sn_5O_{10}.5H_2O$. If more strongly heated, it assumes a yellowish colour, and a hardness resembling that of powdered tin-stone. *Putty powder*, used for polishing, consists of metastannic acid; as found in commerce it generally contains much oxide of lead. Metastannic acid is insoluble in water and diluted acids, and when *fused* with hydrated alkalies, is converted into a soluble stannate; but if *boiled* with solution of potash it is dissolved in the form of metastannate of potash, which will not crystallise, like the stannate, but is obtained as a granular precipitate by dissolving hydrate of potash in its solution. This precipitate has the composition $K_2O.Sn_5O_{10}.4Aq.$; it is very soluble in water, and is strongly alkaline. When it is heated to expel the

water, it is decomposed, and the potash may be washed out with water, leaving metastannic acid. The hydrated metastannic acid may be distinguished from hydrated stannic acid by the action of protochloride of tin, which converts it into the yellow metastannate of tin ($SnO.Sn_5O_{10}.4Aq.$).

Stannate of tin is obtained as a yellowish hydrate by boiling protochloride of tin with hydrated sesquioxide of iron; $Fe_2O_3 + 2SnCl_2 = SnO.SnO_2 + 2FeCl_2$. It is sometimes written Sn_2O_3, and called *sesquioxide of tin.*

282. CHLORIDES OF TIN.—The two chlorides of tin correspond in composition to the oxides.

Stannous chloride, or *protochloride of tin* ($SnCl_2$), is much used by dyers and calico-printers, and is prepared by dissolving tin in hydrochloric acid, when it is deposited, on cooling, in lustrous prismatic needles ($SnCl_2.2Aq.$), known as *tin crystals* or *salts of tin.* The solution of the tin is generally effected in a copper vessel, in order to accelerate the action by forming a voltaic couple, of which the tin is the attacked metal. When gently heated, the crystals lose their water, and are partly decomposed, some hydrochloric acid being evolved ($SnCl_2 + H_2O = SnO + 2HCl$); but, at a higher temperature, a great part of the chloride may be distilled in the anhydrous state; the anhydrous chloride is generally prepared by distilling powdered tin with corrosive sublimate, when it remains in the retort as a brilliant grey solid, which requires a bright red heat to convert it into vapour. When water is poured upon the crystals of stannous chloride, they are only partially dissolved, a white oxychloride of tin ($SnCl_2.SnO.2Aq.$) being separated. A moderately dilute solution of stannous chloride absorbs oxygen from the air, and deposits a white compound of perchloride and binoxide of tin; $2SnCl_2 + O_2 = SnCl_4.SnO_2$. If the solution contains much free hydrochloric acid it remains clear, being entirely converted into perchloride of tin. A strong solution of the chloride is not oxidised by the air, and the weak solution may be longer preserved in contact with metallic tin. Stannous chloride has a great attraction for chlorine as well as for oxygen, and is frequently employed as a deoxidising or dechlorinating agent. Tin may be precipitated from stannous chloride by the action of zinc, in the form of minute crystals. A very beautiful *tin tree* is obtained by dissolving granulated tin in strong hydrochloric acid, with the aid of heat, in the proportion of 8 measured oz. of acid to 1000 grs. of tin, diluting the solution with four times its bulk of water, and introducing a piece of zinc.

Stannic chloride, or *bichloride*, or *tetrachloride of tin* ($SnCl_4$), is obtained in solution when tin is heated with hydrochloric and nitric acids; for the use of the dyer, the solution (*nitromuriate of tin*) is generally made with hydrochlorate of ammonia (sal-ammoniac) and nitric acid. The anhydrous perchloride is obtained by heating tin in a current of dry chlorine, when combination takes place with combustion, and the perchloride distils over as a heavy (sp. gr. 2·28) colourless liquid, volatile (boiling point, 240° F.), and giving suffocating white fumes in the air. When mixed with a little water, energetic combination takes place, and a crystalline hydrate ($SnCl_4.5Aq.$) is formed, which is decomposed by an excess of water, with separation of hydrated stannic acid. Stannic chloride forms crystallisable double salts with the alkaline chlorides. *Pink salt*, used by dyers, is a compound of stannic chloride with hydrochlorate of ammonia $2(NH_3.HCl).SnCl_4$.

283. *Sulphides of tin.*—The *protosulphide*, or *stannous sulphide* (SnS), is found in Cornwall as *tin pyrites*, and may be easily prepared by heating

tin with sulphur, when it forms a grey crystalline mass. It is also obtained as a dark brown precipitate by the action of hydrosulphuric acid upon a solution of stannous chloride. Protosulphide of tin is a sulphur-base, but it may be dissolved by alkalies if some sulphur be added, which converts it into the bisulphide, a decided sulphur acid.

Bisulphide of tin, or *stannic sulphide* (SnS_2), is commonly known as *mosaic gold* or *bronze powder*,* and is used for decorative purposes. It is prepared by a curious process, which was devised in 1771, and must have been the result of a number of trials. 12 parts by weight of tin are dissolved in 6 parts of mercury; the brittle amalgam thus obtained is powdered and mixed with 7 parts of sulphur and 6 of sal-ammoniac. The mixture is introduced into a Florence flask, which is gently heated in a sand-bath as long as any smell of hydrosulphuric acid is evolved; the temperature is then raised to dull redness until no more fumes are disengaged. The mosaic gold is found in beautiful yellow scales at the bottom of the flask, and sulphide of mercury and calomel are deposited in the neck. The mercury appears to be used for effecting the fine division of the tin, and the sal-ammoniac to keep down the temperature (by its volatilisation) below the point at which the bisulphide of tin is converted into protosulphide.

Mosaic gold, like gold itself, is not dissolved by hydrochloric or nitric acid, but easily by *aqua regia*. Alkalies also dissolve it when heated, since the bisulphide of tin is a sulphur acid. On adding hydrosulphuric acid to a solution of stannic chloride, the stannic sulphide is obtained as a yellow precipitate.

284. TITANIUM (Ti = 50 parts by weight), which stands in close chemical relationship to tin, used to be described as a very rare metal, but it has lately been found to exist in considerable quantity in iron ores and clays, although no very important practical application has hitherto been found for it. The form in which it is generally found is *titanic acid* (TiO_2), which occurs uncombined in the minerals *rutile*, *anatase*, and *brookite*, the first of which is isomorphous with tin-stone, and is extremely hard like that mineral. In combination with oxide of iron, titanic acid is found in *iron-sand*, *iserine*, or *menachanite* (found originally at Menachan in Cornwall), which resembles gunpowder in appearance, and is now imported in abundance from Nova Scotia and New Zealand. Some specimens of this mineral contain 40 per cent. of titanic acid, combined with protoxide of iron. To extract titanic acid from it, the finely ground mineral is fused with three parts of carbonate of potash, when carbonic acid is expelled and titanate of potash formed; on washing the mass with hot water, this salt is decomposed, a part of its alkali being removed by the water, and an acid titanate of potash left, mixed with the oxide of iron. This is dissolved in hydrochloric acid, and the solution evaporated to dryness, when the titanic acid, and any silicic acid which may be present, are converted into the insoluble modifications, and are left on digesting the residue again with dilute hydrochloric acid; the residue is washed with water (by decantation, for titanic acid easily passes through the filter), dried, and fused at a gentle heat with bisulphate of potash. The sulphuric acid forms a soluble compound with the titanic acid ($TiO_2.SO_3$), which may be extracted by cold water, leaving the silicic acid undissolved. The solution containing the titanic acid is mixed with about twenty times its volume of water, and boiled for some time, when the titanic acid is separated as a white precipitate, exhibiting a great disposition to cling as a film to the surface of the flask in which the solution is boiled, and giving it the appearance of being corroded. The titanic acid becomes yellow when strongly heated, and white again on cooling; it does not dissolve in solution of potash like silica, but when fused with potash it forms a titanate, which is decomposed by water; the acid titanate of potash which is left may be dissolved in hydrochloric acid, and if the solution be neutralised with carbonate of ammonia, hydrated titanic acid is precipitated, very much resembling

* Bronze powder is also made by powdering finally laminated alloys of copper and zinc, a little oil being used to prevent oxidation.

alumina in appearance. By dissolving the gelatinous hydrate in cold hydrochloric acid, and dialysing, a solution of titanic acid in water is obtained, which is liable to gelatinise spontaneously if it contain more than one per cent. of the acid.

Titanic acid is employed in the manufacture of artificial teeth, and for imparting a straw-yellow tint to the glaze of porcelain.

If a mixture of titanic acid and charcoal be heated to redness in a porcelain tube, through which dry chlorine is passed, *tetrachloride of titanium* ($TiCl_4$) is obtained as a colourless volatile liquid, very similar to perchloride of tin. By passing the vapour of the tetrachloride of titanium over heated sodium, the *metallic titanium* is obtained in prismatic crystals resembling specular iron ore in appearance. Like tin, it is said to dissolve in hydrochloric acid with liberation of hydrogen. The most remarkable chemical feature of titanium is its direct attraction for nitrogen, with which it combines when strongly heated in air. By passing ammonia gas over titanic acid heated to redness, a violet powder is formed, which is a nitride of titanium (TiN_2). Beautiful cubes of a copper colour and great hardness, formerly believed to be metallic titanium, are found adhering to the slags of blast-furnaces in which titaniferous iron ores are smelted; these contain about 77 per cent. of titanium, 18 of nitrogen, and rather less than 4 of carbon, and are believed to consist of a compound of cyanide with nitride of titanium, $TiCy_2.3Ti_3N_2$. A similar compound is obtained by passing nitrogen over a mixture of titanic acid and charcoal heated to whiteness.

Violet-coloured crystals of terchloride of titanium ($TiCl_3$), are obtained by passing hydrogen charged with vapour of tetrachloride of titanium through a red-hot porcelain tube; it forms a violet solution in water, which resembles stannous chloride in its reducing properties.

When a solution of titanic acid (or acid titanate of potash) in hydrochloric acid is acted on by zinc, a violet solution is formed, which deposits, after a time, a blue (or green) precipitate, which appears to be a *sesquioxide of titanium* (Ti_2O_3), and rapidly absorbs oxygen from the air, being converted into titanic acid. A *protoxide of titanium* (TiO) is said to be obtained as a black powder when titanic acid is strongly heated in a crucible lined with charcoal.

Bisulphide of titanium is not precipitated, like bisulphide of tin, when hydrosulphuric acid acts upon the tetrachloride; but if a mixture of the vapour of tetrachloride of titanium with hydrosulphuric acid is passed through a red-hot tube, greenish-yellow scales of the bisulphide, resembling mosaic gold, are deposited.

Titanium, like tin, is classed among the tretratomic elements.

285. TUNGSTEN ($W = 184$) is chiefly found in the mineral *wolfram*, which occurs, often associated with tin-stone, in large brown shining prismatic crystals, which are even heavier than tin-stone (sp. gr. 7·3), from which circumstance the metal derives its name, tungsten, in Swedish, meaning heavy stone. The symbol (W) used for tungsten is derived from the Latin name *wolframium.* Wolfram contains the tungstates of iron and manganese in somewhat variable proportions, but its general composition is expressed by the formula $MnO.WO_3.3(FeO.WO_3)$. *Scheelite*, tungstate of lime ($CaO.WO_3$), is another mineral in which tungsten is found. A tungstate of copper has been found in Chili.

Tungstate of soda is employed by calico-printers as a mordant, and is sometimes applied to muslin, in order to render it uninflammable. It is obtained by fusing wolfram with carbonate of soda, an operation to which tin ores containing this mineral in large quantity are sometimes submitted previously to smelting them. Water extracts the tungstate of soda, which may be crystallised in rhomboidal plates having the composition $Na_2O.WO_3$, 2Aq. When a solution of this salt is mixed with an excess of hydrochloric acid, white *hydrated tungstic acid* ($H_2O.WO_3$.Aq.) is precipitated; but if dilute hydrochloric acid be carefully added to a 5 per cent. solution of tungstate of soda, in sufficient proportion to neutralise the alkali, and the solution be then dialysed (p. 111), the chloride of sodium passes through, and a pure aqueous solution of tungstic acid is left in the dialyser. This solution is unchanged by boiling, and when evaporated to dryness, it forms vitreous scales, like gelatine, which adhere very strongly to the dish. It redissolves in one-fourth of its weight of water, forming a solution of the very high specific gravity 3·2, which is, therefore, able to float glass. The solution has a bitter and astringent taste, and decomposes carbonate of soda with effervescence. It becomes green when exposed to air, from the deoxidising action of organic dust. When the hydrated tungstic acid is heated, it loses water, and becomes of a straw-yellow colour and insoluble in acids. There are at least two modifications of tungstic acid, which bear to each other a relation similar to that between stannic and metastannic acids.

Tungstate of baryta has been employed as a substitute for white lead in painting.

The most characteristic property of tungstic acid is that of yielding a blue oxide ($WO_2.WO_3$), when placed in contact with hydrochloric acid and metallic zinc.

A very remarkable compound containing tungstic acid and soda is obtained when bitungstate of soda ($Na_2O.2WO_3.4H_2O$) is fused with tin. If the fused mass be treated with strong potash, to remove free tungstic acid, washed with water, and treated with hydrochloric acid, yellow lustrous cubical crystals are obtained, which are remarkable, among sodium compounds, for their resistance to the action of water, of alkalies, and of all acids except hydrofluoric. The composition of these crystals appears to be $Na_2O.WO_2.2WO_3$.

The *binoxide of tungsten* (WO_2) appears to be an indifferent oxide, and is obtained by reducing tungstic acid with hydrogen at a low red heat, when it forms a brown powder which is dissolved by boiling in solution of potash, hydrogen being evolved, and tungstate of potash formed.

Metallic tungsten is obtained by reducing tungstic acid with charcoal at a white heat, as an iron-grey infusible metal of sp. gr. 17·6, very hard, not affected by hydrochloric or diluted sulphuric acid, but converted into tungstic acid by the action of nitric acid. When tungsten is dissolved in about ten times its weight of fused steel, it forms an extremely hard alloy.

When tungsten is heated in chlorine, the *tungstic chloride* (WCl_6) sublimes in bronze coloured needles, which are decomposed by water. When gently heated in hydrogen, it is converted into the tetrachloride (WCl_4), but if its vapour be mixed with hydrogen and passed through a glass tube heated to redness, metallic tungsten is obtained in a form in which it is not dissolved even by aqua regia, though it may be converted into tungstate of potash by hypochlorite of potash mixed with potash in excess.

Bisulphide of tungsten (WS_2) is a black crystalline substance resembling plumbago, obtained by heating a mixture of bitungstate of potash with sulphur, and washing with hot water. Tersulphide of tungsten (WS_3) is a sulphur-acid, obtainable as a brown precipitate by dissolving tungstic acid in an alkaline sulphide, and precipitating by an acid.

286. MOLYBDENUM (Mo = 96) derives its name from μολύβδαινα, *lead*, on account of the resemblance of its chief ore, *molybdena*, to black lead. Molybdena is the *bisulphide of molybdenum* (MoS_2), and is found chiefly in Bohemia and Sweden ; it may be recognised by its remarkable similarity to plumbago, and by its giving a blue solution when boiled with strong sulphuric acid. It is chiefly employed for the preparation of molybdate of ammonia, which is used in testing for phosphoric acid. For this purpose the bisulphide of molybdenum is roasted in air at a dull red heat, when sulphurous acid is evolved, and *molybdic acid* (MoO_3) mixed with oxide of iron is left. The residue is digested with strong ammonia, which dissolves the molybdic acid in the form of *molybdate of ammonia*, obtainable in prismatic crystals on evaporation. When a solution of molybdate of ammonia is added to a phosphate dissolved in diluted nitric acid, a yellow precipitate of *phosphomolybdate of ammonia* is produced, which contains molybdic and phosphoric acids combined with ammonia, by the formation of which very minute quantities of phosphoric acid can be detected. If hydrochloric acid be added in small quantity to a strong solution of molybdate of ammonia, the molybdic acid is precipitated, but it is dissolved by an excess of hydrochloric acid, and if the solution be dialysed, the molybdic acid is obtained in the form of an aqueous solution which reddens blue litmus, has an astringent taste, and leaves a soluble gum-like residue when evaporated. Molybdic acid fuses at a red heat to a yellow glass, and may be sublimed in a current of air in shining needles. In contact with diluted hydrochloric acid and metallic zinc, it is converted into a blue compound of molybdic acid with binoxide of molybdenum ($MoO_2.4MoO_3$) which is soluble in water, but is precipitated on adding a saline solution. *Molybdate of lead* ($PbO.MoO_3$) is found as a yellow crystalline mineral. The *binoxide of molybdenum* (MoO_2) is basic, and forms dark red-brown salts. *Protoxide of molybdenum* (MoO) is obtained by adding an alkali to the solution resulting from the prolonged action of zinc upon a hydrochloric solution of molybdic acid. It is a basic oxide which absorbs oxygen from the air.

Metallic molybdenum is obtained by reducing molybdic acid with charcoal at a white heat, as a white metal, fusible with difficulty, unacted upon by hydrochloric and diluted sulphuric acids, but converted into molybdic acid by boiling with nitric acid. It is rather a light metal, its specific gravity being 8·62. When heated in chlorine it yields *tetrachloride of molybdenum* ($MoCl_4$), which forms a red vapour, and condenses in crystals resembling iodine, soluble in water. A *bichloride* ($MoCl_2$) is also known. The *tersulphide* (MoS_3) and *tetrasulphide* (MoS_4) of molybdenum are sulphur-acids.

In addition to the natural sources of molybdenum above mentioned, there may be noticed *molybdic ochre* (an impure molybdic acid), and the difficultly fusible masses called *bear*, from the copper works in Saxony, which contain a large amount of molybdenum combined with iron, copper, cobalt, and nickel.

287. VANADIUM* ($V = 51 \cdot 3$) was originally discovered in certain Swedish iron ores, but its chief ore is the *vanadiate of lead*, which is found in Scotland, Mexico, and Chili. Vanadic acid has also been found in some clays, in the cupriferous sandstone at Perm in Russia, and Alderley Edge in Cheshire. By treating the vanadiate of lead with nitric acid, expelling the excess of acid by evaporation, and washing out the nitrate of lead with water, impure *vanadic acid* (V_2O_5) is obtained, which may be purified by dissolving in ammonia, crystallising the vanadiate of ammonia, and decomposing it by heat, when vanadic acid is left as a reddish-yellow fusible solid, which crystallises on cooling, and dissolves sparingly in water, giving a yellow solution. It dissolves in hydrochloric acid, and if the solution be treated with a reducing agent (such as hydrosulphuric acid) it assumes a fine blue colour. If a solution of vanadiate of ammonia be mixed with tincture of galls, it gives an intensely black fluid, which forms an excellent ink, for it is not bleached by acids (which turn it blue), alkalies, or chlorine.

Vanadium itself has not been obtained. Berzelius endeavoured to procure it by heating vanadic acid with potassium, but Roscoe, who has carefully investigated the vanadium compounds, has shown that the apparently metallic powder thus obtained is really an oxide (V_2O_2).

The oxides of vanadium correspond in composition to those of nitrogen (omitting N_2O). V_2O_2 is a basic oxide, forming salts which give lavender-coloured solutions; these absorb oxygen rapidly from the air, and act as powerful reducing agents. V_2O_3 is a black crystalline body resembling plumbago, and capable of conducting electricity, obtained by heating vanadic acid in a current of hydrogen; it is a basic oxide. V_2O_4 is produced when V_2O_3 is heated in air; it also plays the part of a base, yielding blue salts. Vanadic acid, V_2O_5, forms purple and green compounds with the above oxides. The yellow fuming liquid formerly called chloride of vanadium is really an oxychloride $VOCl_3$. The oxychlorides V_2O_2Cl, $VOCl$, and $VOCl_2$, have also been obtained. There are two compounds of vanadium with nitrogen, VN and VN_2. It will be remarked that the composition of the compounds of vanadium connects this metal with nitrogen, phosphorus, and arsenic.

288. *Niobium* ($Nb = 94$) (formerly called *columbium*) has been obtained from a rare dark grey hard crystalline mineral known as *columbite*, occurring in Massachusetts. This mineral contains *niobic acid* (NbO_2) combined with the oxides of iron and manganese.

The niobic acid is extracted by a laborious process, and forms a white powder sparingly soluble in hydrochloric acid. Niobium itself has been obtained as a black powder insoluble in nitric acid and in aqua regia, but dissolved by a mixture of nitric and hydrofluoric acids.

Tantalum, formerly believed to be identical with niobium, occurs in the *tantalite* and *yttrotantalite* of Sweden, which contain *tantalic acid* (TaO_2)† resembling niobic acid.

Niobium and tantalum have recently been found to the amount of 2 or 3 per cent. in the tin ore of Montebras.

PLATINUM.

$Pt = 197 \cdot 1$ parts by weight.

289. Platinum (*platina*, Spanish diminutive of silver) is always found in the metallic state, distributed in flattened grains through alluvial deposits similar to those in which gold is found; indeed, these grains are generally accompanied by grains of gold, and of a group of very rare metals only found in platinum ores, viz., palladium, iridium, osmium, rhodium, and ruthenium. Russia furnishes the largest supply of platinum from the Ural Mountains, but smaller quantities are obtained from Brazil, Peru, Borneo, Australia, and California.

The process for obtaining the platinum in a marketable form is rather

* *Vanadis*, a Scandinavian deity.

† Ta_2O_5, according to more recent experiments.

a chemical than a metallurgic operation. The ore, containing the grains of platinum and the associated metals, is heated with a dilute mixture of hydrochloric and nitric acids, by which the platinum is converted into perchloride of platinum ($PtCl_4$) and dissolved, whilst the iridium and osmium are left in the residue. The solution is then mixed with some chloride of ammonium, which combines with the perchloride of platinum to form a yellow insoluble salt (ammonio-chloride of platinum, $2(NH_3.HCl).PtCl_4$). This precipitate is collected, washed, and heated to redness, when all its constituents, except the platinum, are expelled in the form of gas, that metal being left in the peculiar-porous condition in which it is known as *spongy platinum*. To convert this into compact platinum is by no means an easy task, on account of the infusibility of the metal, for it remains solid at the very highest temperatures of our furnaces. The spongy platinum is finely powdered in a wooden mortar (as it would cohere into metallic spangles in one of a harder material) and rubbed to a paste with water; this paste is then rubbed through a sieve to render it perfectly smooth and uniform, and introduced into a cylinder of brass, in which it is subjected to pressure so as to squeeze out the water and cause the minute particles of platinum to cohere into a somewhat compact disk; this disk is then heated to whiteness and beaten into a compact metallic ingot by a heavy hammer; it is then ready for forging.

A more modern process for obtaining platinum from its ores is based upon the tendency of this metal to dissolve in melted lead. The platinum ore is fused in a small reverberatory furnace, with an equal weight of sulphide of lead and the same quantity of oxide of lead, when the sulphur and oxygen escape as sulphurous acid, and the reduced lead dissolves the platinum, leaving undissolved a very heavy alloy of osmium and iridium which sinks to the bottom. The upper part of the alloy of lead and platinum is then ladled out and cupelled (page 351), when the latter metal is left in a spongy condition, the lead being removed in the form of oxide. The platinum is then fused by the aid of the oxyhydrogen blowpipe, in a furnace made of lime (fig. 276), whence it is poured into an ingot mould made of gas-carbon. The melted platinum absorbs oxygen mechanically like melted silver, and evolves it again on cooling (see page 352). Platinum articles are now frequently made from the fused metal, instead of from that which has been welded.

Its resistance to the action of high temperatures and of most chemical agents, renders platinum of the greatest service in chemical operations. It will be remembered that platinum stills are employed, even on the large scale, for the concentration of sulphuric acid. In the form of basins, small crucibles, foil, and wire, this metal is indispensable to the analytical chemist. Unfortunately, it is softer than silver, and therefore ill adapted for wear, and is so heavy (sp. gr. 21·5) that even small vessels must be made very thin in order not to be too heavy for a delicate balance. Since it expands less than any other metal when heated, wires of platinum may be sealed into glass without danger of splitting it by unequal expansion. Its malleability and ductility are very considerable, so that it is easily rolled into thin foil and

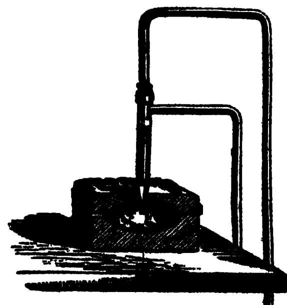


Fig. 276.

drawn into fine wires; in ductility it is surpassed only by gold and silver, and it has been drawn, by an ingenious contrivance of Wollaston's, into wire of only $\frac{1}{3000}$th of an inch in diameter, a mile of which (notwithstanding the high specific gravity of the metal) would only weigh a single grain. This remarkable extension of the metal was effected by casting a cylinder of silver around a very thin platinum wire obtained by the ordinary process of wire-drawing; when the cylinder of silver, with the platinum wire in its centre, was itself drawn out into an extremely thin wire, of course the platinum core would have become inconceivably thin, and when the silver casing was dissolved off by nitric acid, this minute filament of platinum was left. Platinum is sometimes employed for the touch-holes of fowling-pieces on account of its resistance to corrosion. A little iridium is sometimes added to platinum in order to increase its elasticity.

The remarkable power possessed by platinum, of inducing chemical combination between oxygen and other gases, has already been noticed. Even the compact metal possesses this property, as may be seen by heating a piece of platinum foil to redness in the flame of a gauze gas-burner, rapidly extinguishing the gas, and turning it on again, when the cold stream of gas will still maintain the metal at a red heat, in consequence of the combination with atmospheric oxygen at the surface of the platinum. A similar experiment may be made by suspending a coil of platinum wire in the flame of a spirit-lamp (fig. 277), and suddenly blowing out the flame when the metal is intensely heated; the wire will continue to glow by inducing the combination of the spirit vapour with oxygen on its surface. By substituting a little ball of spongy platinum for the coil of platinum wire, and mixing some fragrant essential oil with the spirit, an elegant perfuming lamp has been contrived. Upon the same principle an instantaneous light apparatus has been made, in which a jet of hydrogen gas is kindled by falling upon a fragment of cold spongy platinum, which at once ignites it by inducing its combination with the oxygen condensed within the pores of the metal. Spongy platinum is obtained in a very active form by heating the ammonio-chloride of platinum very gently in a stream of coal-gas or hydrogen as long as any fumes of hydrochloric acid are evolved.

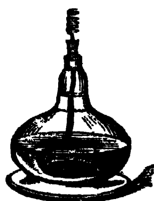


Fig. 277.

If platinum be precipitated in the metallic state from a solution, it is obtained in the form of a sooty powder, called platinum-black, which possesses this power of promoting combination with oxygen in the highest perfection. This form of platinum may be obtained by dissolving the metal in aqua regia, which converts it into perchloride of platinum ($PtCl_4$), evaporating the solution to dryness, and heating the residue gently on a sand-bath as long as it smells strongly of chlorine. The chloride of platinum ($PtCl_2$) thus obtained is dissolved in a strong solution of potash and heated with alcohol, when the platinum-black is precipitated, and must be filtered off, washed, and dried at a gentle heat.

Platinum in this form is capable of absorbing 800 times its volume of oxygen, which does not enter into combination with it, but is simply condensed into its pores, and is available for combination with other bodies. A jet of hydrogen allowed to pass on to a grain or two of this powder is kindled at once, and if a few particles of it be thrown into a mixture of hydrogen and oxygen, explosion immediately follows. A drop

of alcohol is also inflamed when allowed to fall upon a little of the powder. Platinum black loses its activity after having been heated to redness.

Although platinum resists the action of hydrochloric and nitric acids, unless they are mixed, and is unaffected at the ordinary temperature by other chemical agents, it is easily attacked at high temperatures by phosphorus, arsenic, carbon, boron, silicon, and by a large number of the metals; the caustic alkalies and alkaline earths also corrode it, so that some discretion is necessary in the use of vessels made of this costly metal. When platinum is alloyed with 10 parts of silver, both metals may be dissolved by nitric acid.

290. *Oxides of platinum.*—Only one compound of platinum with oxygen is known in the separate state, the other having been obtained in combination with water. The *protoxide*, PtO (*platinous oxide*), is precipitated as a black hydrate by decomposing the protochloride with potash, and neutralising the solution with dilute sulphuric acid. It is a feeble base, and decomposes when heated, leaving metallic platinum. *Binoxide of platinum*, PtO_2 (*platinic oxide*), is also a weak base, but occasionally plays the part of an acid, whence it is sometimes termed platinic acid. *Platinate of soda* ($Na_2O.3PtO_2.6Aq.$) may be crystallised from a solution of the hydrated binoxide in soda. *Platinate of lime* is convenient for the separation of platinum from iridium, which is generally contained in the commercial metal; for this purpose the platinum is dissolved in nitro-hydrochloric acid, the solution evaporated till it solidifies on cooling, the mixed chlorides of iridium and platinum dissolved in water, and decomposed with an excess of lime *without exposure to light;* the platinum then passes into solution as platinate of lime, and the platinic acid may be separated from the filtered solution, though still in combination with lime, by exposure to light. Acids dissolve binoxide of platinum, forming salts of a brown colour which have not been crystallised. If binoxide of platinum be dissolved in diluted sulphuric acid and the solution mixed with excess of ammonia, a black precipitate of *fulminating platinum* is obtained, which detonates violently at about 400° F. This compound is said to have a composition corresponding to the formula $N_2H_2Pt^{iv}.4H_2O$, or a combination of water with a double molecule of ammonia (N_2H_6), in which four atoms of hydrogen are replaced by one atom of tetratomic platinum.

Chlorides of platinum.—The *perchloride*, or *platinic chloride* ($PtCl_4$), is the most useful salt of the metal, and may be prepared by dissolving scraps of platinum foil in a mixture of four measures of hydrochloric acid with one of nitric acid (100 grains of platinum require 2 measured ounces of hydrochloric acid), evaporating the liquid at a gentle heat to the consistence of a syrup, redissolving in hydrochloric acid, and again evaporating to expel excess of nitric acid. The syrupy liquid solidifies on cooling to a red-brown mass, which is very deliquescent, and dissolves easily in water or alcohol to a red-brown solution. If the concentrated solution be allowed to cool before all the free hydrochloric acid has been expelled, long brown prismatic crystals of a combination of the perchloride with hydrochloric acid are obtained ($PtCl_4.2HCl.6Aq.$) The perchloride of platinum is remarkable for its disposition to form sparingly soluble double chlorides with the chlorides of the alkali metals and the hydrochlorates of organic bases, a property of great value to the chemist in effecting the detection and separation of these bodies.

A good example of this has lately been afforded in the separation of potassium, rubidium, and cœsium. The chlorides of these three metals having been separated from the various other salts contained in the mineral water in which they occur, are precipitated with perchloride of platinum, which forms combinations with all the three chlorides. The platino-chloride of potassium is more easily dissolved by boiling water than those of rubidium and cœsium, and is removed by boiling the mixed precipitate with small portions of water as long as the latter acquires a yellow colour. The remaining platino-chlorides of rubidium and cœsium are then heated in a current of hydrogen, which reduces the platinum to the metallic state, and the chlorides may then be extracted by water, in which they are very soluble.

Platino-chloride of potassium ($2KCl,PtCl_4$) forms minute yellow octahedral crystals; those of rubidium and cœsium have a similar composition and crystalline form.

Platino-chloride of sodium differs from these in being very soluble in water and alcohol; it may be crystallised in long red prisms, having the composition ($2NaCl,PtCl_4,6Aq.$)

Ammonio-chloride of platinum ($2NH_3.HCl).PtCl_4$) has been already noticed as the form in which platinum is precipitated in order to separate it from other metals. It crystallises, like the potassium-salt, in yellow octahedra, which are very sparingly soluble in water and insoluble in alcohol. It is the form into which nitrogen is finally converted in analysis in order to determine its weight. When heated to redness, this salt leaves a residue of spongy platinum. The perchloride of platinum is sometimes used for browning gun-barrels, &c., under the name of *muriate of platina.*

Protochloride of platinum or *platinous chloride* ($PtCl_2$).—The perchloride of platinum may be heated to 450° F. without decomposition, but above that temperature it evolves chlorine, and is slowly converted into the protochloride, which is reduced, at a much higher temperature, to the metallic state. Platinous chloride forms a dingy green powder, which is insoluble in water and in nitric and sulphuric acids, but dissolves in hot hydrochloric acid, and in solution of platinic chloride, yielding in the former a bright red, in the latter a very dark brown-red solution. Its solution in hydrochloric acid is not precipitated by chloride of potassium, but a soluble double chloride ($2KCl,PtCl_2$) may be crystallised from the liquid. If hydrochlorate of ammonia be added to the hydrochloric solution, a double salt of hydrochlorate of ammonia with protochloride of platinum $2(NH_3.HCl).PtCl_2$) may be obtained in yellow crystals by evaporation. If, instead of hydrochlorate of ammonia, free ammonia be added in excess to the boiling solution of protochloride of platinum in hydrochloric acid, brilliant green needles (green salt of Magnus) are deposited on cooling, which contain the elements of platinous chloride and ammonia ($PtCl_2(NH_3)_2$, but from the behaviour of this compound with chemical agents, its true formula would appear to be $N_2H_6Pt''Cl_2$, in which the place of two atoms of hydrogen in two molecules of sal-ammoniac is occupied by platinum. By heating this salt with an excess of ammonia, the solution, on cooling, deposits yellowish-white prismatic crystals of *hydrochlorate of diplatosamine;* $N_4H_{10}Pt''.2HCl.Aq.$, the production of which may be represented by the equation—



$$N_2H_6Pt''Cl_2 + 2NH_3 = N_4H_{10}Pt''.2HCl.$$

By decomposing a solution of this salt with sulphate of silver, the *sulphate of diplatosamine* is obtained; $N_4H_{10}Pt''.2HCl + Ag_2O.SO_3 = N_4H_{10}Pt''.H_2O.SO_3 + 2AgCl$.

When the solution of sulphate of diplatosamine is treated with hydrate of baryta, sulphate of baryta is precipitated, and a powerfully alkaline solution is obtained, which yields crystals of *hydrate of diplatosamine* $N_4H_{10}Pt''.2H_2O$, a strong alkali which may be regarded as a compound of water with 4 molecules of ammonia (N_4H_{12}), in which 2 atoms of hydrogen are replaced by platinum. The hydrate of diplatosamine has a strong resemblance to the hydrated mineral alkalies, eagerly absorbing

carbonic acid from the air, and expelling ammonia from its salts. When the hydrate of diplatosamine is heated to 230° F. it gives off water and ammonia, and becomes converted into a grey insoluble substance, which is *hydrate of platosamine*, $N_2H_4Pt''.H_2O$, and may be regarded as a compound of water with a double molecule of ammonia (N_2H_6), in which one-third of the hydrogen is replaced by platinum. This substance is also a base, and forms salts, most of which are insoluble; the *sulphate of platosamine*, $N_2H_4Pt.H_2O.SO_3.Aq.$, may be regarded as sulphate of ammonia ($2NH_3.H_2O.SO_3$), in which two atoms of the hydrogen are replaced by platinum. The *hydrochlorate of platosamine* ($N_2H_4Pt.2HCl$) is isomeric with the green salt of Magnus, and may be obtained from that compound by dissolving it in a hot solution of sulphate of ammonia, from which it crystallises on cooling.*

If the *hydrochlorate of platosamine*, suspended in boiling water, be treated with chlorine, it is converted into *hydrochlorate of platinamine*, $N_2H_2Pt^{iv}.4HCl$, which may be represented as the hydrochlorate of an ammonia, in which 4 atoms of hydrogen have been replaced by 1 atom of platinum in the condition in which it exists in the perchloride ($PtCl_4$), where it is equivalent to H_4. The conversion of the hydrochlorate of platosamine into hydrochlorate of platinamine may be represented by the equation, $N_2H_4Pt.2HCl + Cl_2 = N_2H_2Pt.4HCl$. By boiling the hydrochlorate of platinamine with nitrate of silver, it is converted into *nitrate of platinamine* $N_2H_2Pt(HNO_3)_4$, and when this is dissolved in boiling water and decomposed by ammonia, the *hydrate of platinamine* ($N_2H_2Pt,4H_2O$) is obtained in yellow prismatic crystals, having the same composition as that assigned to fulminating platinum.

Several other platinum compounds derived from ammonia have been obtained, but cannot at present be so conveniently classified. The following table exhibits the composition of those here enumerated, the platinum, as it exists in platinous chloride ($PtCl_2$), occupying the place of 2 atoms of hydrogen, being represented by Pt'', and the platinum, as it exists in platinic chloride ($PtCl_4$) occupying the place of 4 atoms of hydrogen, by Pt^{iv}.

Hydrate of platosamine,	$N_2H_4Pt''.H_2O$
Hydrochlorate of platosamine,	$N_2H_4Pt''.2HCl$
Sulphate of platosamine,	$N_2H_4Pt''.H_2O.SO_3.Aq.$
Hydrate of platinamine,	$N_2H_2Pt^{iv}.4H_2O$
Hydrochlorate of platinamine,	$N_2H_2Pt^{iv}.4HCl$
Hydrate of diplatosamine,	$N_4H_{10}Pt''.2H_2O$
Hydrochlorate of diplatosamine,	$N_4H_{10}Pt''.2HCl.Aq.$
Sulphate of diplatosamine,	$N_4H_{10}Pt''.H_2O.SO_3.$

' Some of the salts of *diplatinamine* ($N_4H_8Pt^{iv}$) have been obtained, this base being derived from 4 molecules of ammonia in which H_4 have been replaced by Pt^{iv}.

The *sulphides of platinum* correspond in composition to the oxides and chlorides, and may be obtained by the action of hydrosulphuric acid upon the respective chlorides, as black precipitates.

291. PALLADIUM (Pd = 106·5) is found in small quantity associated with native gold and platinum. It presents a great general resemblance to platinum, but is distinguished from it by being far more easily oxidised, and by its special attraction for cyanogen, with which it forms an insoluble compound. This circumstance is taken advantage of in separating palladium from the platinum ores, for which purpose the solution from which the greater part of the platinum has been precipitated by hydrochlorate of ammonia (p. 389) is neutralised with carbonate of soda, and mixed with solution of cyanide of mercury $Hg(CN)_2$, when a yellowish precipitate of cyanide of palladium is obtained, yielding spongy palladium when heated, which may be welded into a compact form in the same manner as platinum. When alloyed with native gold, palladium is separated by fusing the alloy with silver, and boiling it with nitric acid, which leaves the gold undissolved. The silver is precipitated from the solution as chloride by adding chloride of sodium, and metallic zinc is placed in the liquid, which precipitates the palladium, lead, and copper, as a black powder. This is dissolved in nitric acid, and the solution mixed with an excess of ammonia, which precipitates the oxide of lead, leaving the copper and palladium in solution. On adding hydrochloric acid in slight excess, a yellow precipitate of *hydrochlorate of*

* The salts of diplatosamine are distinguished from those of platosamine by the action of nitrous acid, which gives a fine blue or green precipitate or coloration with the former. For the cause of this change, and for many other interesting points in the history of these platinum compounds, the reader is referred to the elaborate and accurate memoir by Hadow (Journal of the Chemical Society, August 1866).

palladamine ($N_2H_4Pd,2HCl$) is obtained, which leaves metallic palladium when heated.

Palladium is harder than platinum and much lighter (sp. gr. 11·5); it is malleable and ductile like that metal, and somewhat more fusible, though it cannot be melted in an ordinary furnace.* It is unchangeable in air unless heated, when it becomes blue from superficial oxidation, but regains its whiteness when further heated, the oxide being decomposed. Unlike platinum, it may be dissolved by nitric acid, forming *nitrate of palladium* ($PdO.N_2O_5$), which is sometimes employed in analysis for precipitating iodine from the iodides, in the form of black *iodide of palladium* (PdI_2). Palladium is useful, on account of its hardness, lightness, and resistance to tarnish, in the construction of philosophical instruments; alloyed with twice its weight of silver, it is used for small weights.

Of the *oxides of palladium*, two correspond with those of platinum, and a basic *oxide* (PdO) has been obtained by gently heating the binoxide. *Tetrachloride of palladium* ($PdCl_4$) is very unstable, being easily decomposed, even in solution, into the *bichloride* ($PdCl_2$) and free chlorine. Both the chlorides form double salts with the alkaline chlorides, those containing the *palladious chloride* ($PdCl_2$) having a dark green colour. Pulverulent *carbide of palladium* is formed when the metal is heated in the flame of a spirit-lamp.

292. Rhodium (Ro = 104·3), another of the metals associated with the ores of platinum, has acquired its name from the red colour of many of its salts (*ῥόδον, a rose*). It is obtained from the solution of the ore in *aqua regia* by precipitating the platinum with hydrochlorate of ammonia, neutralising with carbonate of soda, adding cyanide of mercury to separate the palladium, and evaporating the filtered solution to dryness with excess of hydrochloric acid. On treating the residue with alcohol, the double chloride of rhodium and sodium is left undissolved as a red powder. By heating this in a tube through which hydrogen is passed, the rhodium is reduced to the metallic state, and the chloride of sodium may be washed out with water, leaving a grey powder of metallic rhodium, which is fused by the oxyhydrogen blowpipe with greater difficulty than platinum, and forms a very hard malleable metal not dissolved even by *aqua regia*, although this acid dissolves it in the ores of platinum, because it is alloyed with other metals. If platinum be alloyed with 30 per cent. of rhodium, however, it is not affected by *aqua regia*, which will probably render the alloy useful for chemical vessels. Rhodium may be brought into solution by fusing it with bisulphate of potash, when sulphurous acid escapes, and a double sulphate of rhodium and potash is formed, which gives a pink solution with water. Finely divided rhodium is oxidised when heated in air. It appears to form two oxides, the *protoxide* (RoO), which is very little known, and the *sesquioxide* (Ro_2O_3), obtained by fusing rhodium with carbonate of potash and nitre, and washing the fused mass with water, which leaves an insoluble compound of the sesquioxide with potash; on treating this with hydrochloric acid, the sesquioxide of rhodium is left. It is not decomposed by heat, and is insoluble in acids, though it is a basic oxide, and its salts, which have a red colour, are obtained by indirect methods.

Terchloride of rhodium ($RoCl_3$) has a brownish black colour, and does not crystallise. Its aqueous solution is red, and it forms crystallisable double salts with the alkaline chlorides, which have a fine red colour. The double chloride of rhodium and sodium, ($3NaCl.RoCl_3$).9Aq., is prepared by heating a mixture of pulverulent rhodium and chloride of sodium in a current of chlorine. It crystallises in red octahedra. On boiling a solution of terchloride of rhodium with ammonia in excess, a yellow ammoniated salt ($RoCl_3.5NH_3$) may be crystallised out, from which metallic rhodium may be obtained by ignition.

With sulphur, rhodium combines energetically at a high temperature; a protosulphide and a sesquisulphide have been obtained.

An alloy of gold with between 30 and 40 per cent. of rhodium has been found in Mexico.

293. Osmium (Os = 199) is characterised by its yielding a very volatile acid oxide (osmic acid, OsO_4), the vapours of which have a very irritating odour (*ὀσμή, odour*). It occurs in the ores of platinum in flat scales, consisting of an alloy of osmium, iridium, ruthenium, and rhodium. This alloy is also found associated with native

* Palladium, at a slightly elevated temperature, absorbs, mechanically, many times its volume of hydrogen. Hammered palladium foil condenses 640 times its volume of hydrogen, below 212° F., though it has not the power of absorbing oxygen or nitrogen. Foil made from fused palladium only absorbs 68 times its volume of hydrogen.—(Graham, Proc. Roy. Soc., June 1866).

gold, and being very heavy, it accumulates at the bottom of the crucible in which the gold is melted. The osmium alloy is extremely hard, and has been used to tip the points of gold pens. When a grain of it happens to be present in the gold which is being coined, it often seriously injures the die. When the platinum ore is treated with *aqua regia*, this alloy is left undissolved, together with grains of chrome-iron ore and titanic iron. To extract the osmium from this residue, it is heated in a porcelain tube through which a current of dry air is passed, when the osmium is converted into osmic acid, the vapour of which is carried forward by the current of air and condensed in bottles provided to receive it. The *osmic acid* forms colourless prismatic crystals which fuse and volatilise below the boiling-point of water, yielding a most irritating vapour resembling chlorine. It is very soluble in water, giving a solution which exhales the odour of the acid and stains the skin black; tincture of galls gives a blue precipitate with the solution. Its acid properties are feeble, for it neither reddens litmus nor decomposes the carbonates, and its salts are decomposed by boiling their solutions. By adding hydrosulphuric acid to a solution of osmic acid, the *tetrasulphide of osmium* (OsS_4) is obtained as a black precipitate, and if this be carefully dried and heated in a crucible made of gas-carbon, *metallic osmium* is obtained as a brittle mass (sp. gr. 21·4), which is not fused even by the oxyhydrogen blowpipe, and is not soluble in acids. When obtained by other processes in a finely divided state, osmium oxidises even at the ordinary temperature, and emits the odour of osmic acid. In this state, also, it may be dissolved by nitric acid, which converts it into osmic acid.

By dissolving osmic acid in potash and adding alcohol, the latter is oxidised at the expense of the osmic acid, and rose-coloured octahedral crystals of *osmite of potash* ($K_2O.OsO_3$, 2Aq.) are obtained; the osmious acid has not been isolated. A protoxide and a binoxide of osmium have been obtained.

Osmium appears to form four chlorides—*bichloride* ($OsCl_2$), *terchloride* ($OsCl_3$), *tetrachloride* ($OsCl_4$), and *hexachloride* ($OsCl_6$). The bichloride and tetrachloride are formed by the direct combination of chlorine with osmium; the former sublimes in green needles, which yield a blue solution in water, soon absorbing oxygen from the air and becoming converted into tetrachloride. By heating a mixture of pulverulent osmium with chloride of potassium in a current of chlorine, a double chloride of osmium and potassium (2KCl, $OsCl_4$) is obtained, which is sparingly soluble, and crystallises in octahedra like the corresponding salt of platinum. When decomposed with nitrate of silver it gives a dark green precipitate (2AgCl, $OsCl_4$).

294. RUTHENIUM (Ru = 104·2).*—In the process for extracting osmium from the residue left on treating the platinum ore with *aqua regia*, by heating in a current of air, square prismatic crystals of *binoxide of ruthenium* (RuO_2) are deposited, nearer to the heated portion of the tube than the osmic acid, for the binoxide is not itself volatile, being only carried forward mechanically in company with the osmic acid. When binoxide of ruthenium is heated in hydrogen, *metallic ruthenium* is obtained as a hard, brittle, almost infusible metal, which is scarcely affected even by *aqua regia*. The *protoxide of ruthenium* (RuO) is a dark grey powder insoluble in acids. The *sesquioxide* (Ru_2O_3) and the *binoxide* (RuO_2) have feebly basic properties. The sesquioxide is not decomposed by heat. The anhydrous binoxide is a greenish blue powder. *Ruthenic acid* (RuO_3) is known only in combination with bases.

295. IRIDIUM (Ir = 197·1), named from *Iris, the rainbow*, in allusion to the varied colours of its compounds, has been mentioned above as occurring in the insoluble alloy from the platinum ores. It is also sometimes found separately, and occasionally alloyed with platinum, the alloy crystallising in octahedra, which are even heavier than platinum (sp. gr. 22·3). If the insoluble osmiridium alloy left by *aqua regia* be mixed with common salt and heated in a current of chlorine, a mixture of the sodio-chlorides of the metals is obtained, and may be extracted by boiling water. If the solution be evaporated and distilled with nitric acid, the osmium is distilled off as osmic acid, and by adding chloride of ammonium to the residual solution, the iridium is precipitated as a dark red-brown ammonio-chloride (($2NH_3$, HCl), $IrCl_4$) which leaves metallic iridium when heated. Like platinum, it then forms a grey spongy mass, but is oxidised when heated in air, and may be fused with the oxy-hydrogen blowpipe to a hard brittle mass (sp. gr. 21·2), which does not oxidise in air. Like rhodium it is not attacked by *aqua regia*, unless alloyed with platinum. The product of the oxidation of finely divided iridium in air is the *sesquioxide* (Ir_2O_3), which is a black powder used for imparting an intense black to porcelain; it is

* A new mineral found in Borneo, and named *laurite*, contains sulphides of ruthenium and osmium. It forms small lustrous granules.

insoluble in acids. The *protoxide* (IrO) is also more easily acted upon by alkalies than by acids; its solution in potash becomes blue when exposed to air, from the formation of the *binoxide* (IrO_2). The *teroxide* (IrO_3) is green. The *bichloride* ($IrCl_2$) and *tetrachloride* ($IrCl_4$) of iridium resemble the corresponding chlorides of platinum in forming double salts with the alkaline chlorides. There is also a *trichloride* ($IrCl_3$), the solution of which has a green colour, and gives a yellow precipitate with mercurous nitrate, and a blue precipitate, soon becoming white, with nitrate of silver. Iridium resembles palladium in its disposition to combine with carbon when heated in the flame of a spirit-lamp.

296. The following table exhibits a general view of the analytical process by which the remarkable metals associated in the ores of platinum may be separated from each other, omitting the minor details which are requisite to ensure the purity of each metal.

Analysis of the Ore of Platinum.

Boil with *aqua regia.*

<table>
<tr><td colspan="3">Dissolved.
PLATINUM, PALLADIUM, RHODIUM.
Add chloride of ammonium.</td><td colspan="4">Undissolved.
IRIDIUM, OSMIUM, RUTHENIUM.
Chrome iron, Titanic iron, &c.
Heat in current of dry air.</td></tr>
<tr><td rowspan="2">Precipitated;
PLATINUM
as
$2NH_4Cl, PtCl_4$.</td><td colspan="2">Solution:
Neutralise with carbonate of soda; add cyanide of mercury.</td><td rowspan="2">Volatilised
OSMIUM
as OsO_4.</td><td rowspan="2">Carried forward by the current;
RUTHENIUM
as RuO_2.</td><td colspan="2">Residue;
Mix with chloride of sodium, and heat in current of chlorine.
Treat with boiling water.</td></tr>
<tr><td>Precipitated;
PALLADIUM
as $PdCy_2$.</td><td>Solution;
Evaporate with hydrochloric acid.
Treat with alcohol.
Insoluble.
RHODIUM
as $3NaCl.RoCl_3$.</td><td>Dissolved.
IRIDIUM
as $2NaCl.IrCl_4$.</td><td>Residue.
Titanic iron,
Chrome iron,
&c.</td></tr>
</table>

The group of *platinoid metals* exhibits some very remarkable features, and it is to be regretted that this group is comparatively imperfectly known in consequence of the difficulty and expense attendant upon the purification of the metals. Its members may be arranged in two divisions, the metals in each agreeing closely in their atomic weights and specific gravities.

	Atomic weight.	Sp. gr.		Atomic weight.	Sp. gr.
Platinum, . .	197·1	21·5	Palladium, .	106·5	11·4
Osmium, . .	199·0	21·4	Rhodium, .	104·3	12·1
Iridium, . .	197·1	21·2	Ruthenium,	104·2	11·4

Through osmium, this group of elements is connected with the group containing antimony, arsenic, and phosphorus, which osmium resembles in the facility with which it is oxidised, and in the volatility of the oxide formed. Palladium connects it with mercury and silver, by its solubility in nitric acid, and its special attraction for cyanogen and iodine.

GOLD.

Au = 196·6 parts by weight.

297. Gold is one of those few metals which are always found in the metallic state, and is remarkable for the extent to which it is distributed, though in small quantities, over the surface of the earth. The principal supplies of this metal are derived from Australia, California, Mexico, Brazil, Peru, and the Uralian Mountains. Small quantities have been occasionally met with in our own islands, particularly at Wicklow, at Cader Idris in Wales, Leadhills in Scotland, and in Cornwall.

The mode of the occurrence of gold in the mineral kingdom resembles that of the ore of tin, for it is either found disseminated in the primitive

rocks, or in alluvial deposits of sand, which appear to have been formed by the disintegration of those rocks under the continued action of torrents. In the former case, the gold is often found crystallised in cubes and octahedra, or in forms derived from these, and sometimes aggregated together in dendritic or branch-like forms. In the alluvial deposits, the gold is usually found in small scales (gold dust), but sometimes in masses of considerable size (nuggets), the rounded appearance of which indicates that they have been subjected to attrition.

The extraction of the particles of gold from the alluvial sands is effected by taking advantage of the high specific gravity of the metal (19·3), which causes it to remain behind, whilst the sand, which is very much lighter (sp. gr. 2·6), is carried away by water. This washing is commonly performed by hand, in wooden or metal bowls, in which the sand is shaken up with water, and the lighter portions dexterously poured off, so as to leave the grains of gold at the bottom of the vessel. On a somewhat larger scale, the auriferous sand is washed in a cradle or inclined wooden trough, furnished with rockers, and with an opening at the lower end for the escape of the water. The sand is thrown on to a grating at the head of the cradle, which retains the large pebbles, whilst the sand and gold pass through, the former being washed away by a stream of water which is kept flowing through the trough.

When the gold is disseminated through masses of quartz or other rock, much labour is expended in crushing the latter before the gold can be separated. This is effected either by passing the coarse fragments between heavy rollers of hard cast-iron, or by stamping them, with wooden beams shod with iron, in troughs through which water is kept continually flowing.

In some cases it is found advantageous to smelt the ore by fusing it with some substance capable of uniting with the gold, and of being afterwards readily separated from it. Lead is peculiarly adapted for this purpose; the crushed ore, being mixed with a suitable proportion, either of metallic lead, or of litharge (oxide of lead) and charcoal, or even of galena (sulphide of lead), together with some lime and oxide of iron or clay, to flux the silica, is fused on the hearth of a reverberatory furnace, when the fused lead dissolves the particles of gold, and collects beneath the lighter slag. The lead is afterwards separated from the gold by cupellation (see p. 351.)

In smelting the ores of gold in Hungary, the metal is concentrated by means of sulphide of iron. The ore consists of quartz and iron pyrites (bisulphide of iron) containing a little gold. On fusing the crushed ore with lime, to flux the quartz, the pyrites loses half its sulphur, and becomes sulphide of iron (FeS), which fuses and sinks below the slag, carrying with it the whole of the gold. If this product be roasted so as to convert the iron into oxide, and be then again fused with a fresh portion of the ore, the oxide of iron will flux the quartz, whilst the fresh portion of sulphide of iron will carry down the whole of the gold contained in both quantities of ore. This operation having been repeated until the sulphide of iron is rich in gold, it is fused with a certain quantity of lead, which extracts the gold and falls to the bottom. The lead is then cupelled in order to obtain the gold.

When the ores of lead, silver, or copper contain gold, it is always found to have accompanied the silver extracted from them, and is separated from it by a process to be presently noticed.

Gold is sometimes separated from the impurities remaining with it after extraction by washing, by the process of amalgamation, which consists in shaking the mixture with mercury in order to dissolve the gold-dust, and straining the liquid amalgam through a chamois leather, which allows the excess of mercury to pass through, but retains the solid portion containing the gold, from which the mercury is then separated by distillation.*

In the Tyrol, this process is adopted for separating the gold from an auriferous iron pyrites, by grinding it in a mill of peculiar construction, with water and a little mercury, the latter being allowed to act upon successive portions of ore until it becomes sufficiently rich to be strained and distilled.

Gold, as found in nature, is generally alloyed with variable proportions of silver and copper, the separation of which is the object of the gold refiner. It may be effected by means of nitric acid, which will dissolve the silver and copper, provided that they do not bear too small a proportion to the gold. Sulphuric acid, however, being very much cheaper, is generally employed. The alloy is fused and poured into water, so as to granulate it and expose a larger surface to the action of the acid; it is then boiled with concentrated sulphuric acid (oil of vitriol), which converts the silver and the copper into sulphates, with evolution of sulphurous acid gas, whilst the gold is left untouched. In order to recover the silver from the solution of the sulphates in water, scraps of copper are introduced into it, when that metal decomposes the sulphate of silver, producing sulphate of copper, and causing the deposition of the silver in the metallic state. Finally, the sulphate of copper may be obtained from the solution by evaporation and crystallisation. This process is so effectual when the proportion of gold in an alloy is very small, that even $\frac{1}{20}$th part of this metal may be profitably extracted from 100 parts of an alloy, and much gold has been obtained in this way from old silver plate, coins, &c., which were manufactured before so perfect a process for the separation of these metals was known. On boiling old silver coins or ornaments with nitric acid, they are generally found to yield a minute proportion of gold in the form of a purple powder. But this plan of separation is not so successful when the alloy contains a very large quantity of gold, for the latter metal seems to protect the copper and silver from the solvent action of the acid. Thus, if the alloy contains more than $\frac{1}{5}$th of its weight of gold, it is customary to fuse it with a quantity of silver, so as to reduce the proportion of gold below that point, before boiling it with the acid. Again, if the alloy contains a large quantity of copper, it is found expedient to remove a great deal of this metal in the form of oxide by heating the alloy in a current of air.

Gold which is brittle and unfit for coining, in consequence of the presence of small quantities of foreign metals, is sometimes refined by melting it with oxide of copper or with a mixture of nitre and borax, when the foreign metals, with the exception of silver, are oxidised and dissolved in the slag. Another process consists in throwing some corrosive sublimate (chloride of mercury) into the melting pot, and stirring it up with the metal, when its vapour converts the metallic impurities into chlorides, which are volatilised. An excellent method, devised by F. B. Miller of Sydney, consists in fusing the gold with a little borax, and passing chlo-

* A small quantity of sodium dissolved in the mercury has been found very materially to facilitate the amalgamation of gold and silver ores, apparently because the amalgam of sodium is more highly electropositive than mercury, in relation to the gold.

rine gas into it through a clay tube. Antimony, arsenic, &c., are carried off as chlorides, whilst the silver, also converted into chloride, rises to the surface of the gold in a fused state, afterwards solidifying into a cake, which is reduced to the metallic state by placing it between plates of wrought-iron and immersing it in diluted sulphuric acid.

Pure gold, like pure silver, is too soft to resist the wear to which it is subjected in its ordinary uses, and it is therefore alloyed for coinage in this country with $\frac{1}{11}$th of its weight of copper, so that gold coin contains 1 part of copper and 11 parts of gold. The gold used for articles of jewellery is alloyed with variable proportions of copper and silver. The alloy of copper and gold is much redder than pure gold.

The degree of purity of gold is generally expressed by quoting it as of so many carats fine. Thus, pure gold is said to be 24 carats fine; English standard gold is 22 carats fine, that is, contains 22 carats of gold out of the 24. Gold of 18 carats fine would contain 18 parts of gold out of the 24, or $\frac{3}{4}$ths of its weight of gold.

Pure gold is easily prepared from standard or jeweller's gold, by dissolving it in hydrochloric acid mixed with one-fourth of its volume of nitric acid, evaporating the solution to a small bulk to expel excess of acid, diluting with a considerable quantity of water, filtering from the separated chloride of silver, and adding a solution of sulphate of iron, when the gold is precipitated as a dark purple powder, which may be collected on a filter, well washed, dried, and fused in a small French clay crucible with a little borax, the crucible having been previously dipped in a hot saturated solution of borax, and dried, to prevent adhesion of the globules of gold. The action of the sulphate of iron upon the terchloride of gold is explained by the equation—



$$2AuCl_3 + 6(FeO.SO_3) = Au_2 + Fe_2Cl_6 + 2(Fe_2O_3.3SO_3).$$

By employing oxalic acid instead of sulphate of iron, and heating the solution, the gold is precipitated in a spongy state, and becomes a coherent lustrous mass under pressure. The metal is employed in this form by dentists.

When standard gold is being dissolved in *aqua regia*, it sometimes becomes coated with a film of chloride of silver which stops the action of the acid; the liquid must then be poured off, the metal washed, and treated with ammonia, which dissolves the chloride of silver; the ammonia must be washed away before the metal is replaced in the acid. In the case of jeweller's gold, it is advisable to extract as much silver and copper as possible by boiling it with nitric acid, before attempting to dissolve the gold. Gold lace should be incinerated to get rid of the cotton before being treated with acid.

The genuineness of gold trinkets, &c., is generally tested by touching them with nitric acid, which attacks them if they contain a very considerable proportion of copper, producing a green stain, but this test is evidently useless if the surface be gilt. The weight is, of course, a good criterion in practised hands, but even these have been deceived by bars of platinum covered with gold. The specific gravity may be taken in doubtful cases; that of sovereign gold is 17·157.

In *assaying gold*, the metal is wrapped in a piece of thin paper together with about three times its weight of pure silver, and added to twelve times its weight of pure lead fused in a bone-ash *cupel* (see page 352) placed in a muffle (or exposed to a strong oxidising blowpipe flame), when the lead and copper are oxidised, and the fused oxide of lead dissolves that of copper, both being absorbed by the cupel. When the metallic button no longer diminishes in size, it is allowed to cool, hammered into a flat disk which is annealed by being heated to redness, and rolled out to a thin plate, so that it may be rolled up by the thumb and finger into a *cornette* which is boiled with nitric acid (sp. gr. 1·18) to extract the silver; the remaining gold is washed with distilled water, and boiled with nitric acid of sp. gr. 1·28, to extract the last traces of silver, after which it is again washed, heated to redness in a small crucible, and weighed.

The stronger nitric acid could not be used at first, since it would be likely to break the cornet into fragments which could not be so readily washed without loss. The addition of the three parts of silver (*quartation*) is made in order to divide the alloy, and permit the easy extraction of the silver by nitric acid, which cannot be effected when the gold predominates.

298. The physical characters of gold render it very conspicuous among the metals; it is the heaviest of the metals in common use, with the exception of platinum, its specific gravity being 19·3. In malleability and ductility it surpasses all other metals; the former property is turned to advantage for the manufacture of gold leaf, for which purpose a bar of gold is passed between rollers which extend it into the form of a riband; this is cut up into squares, which are packed between layers of fine vellum, and beaten with a heavy hammer; these thinner squares are then again cut up and beaten between layers of gold-beater's skin until they are sufficiently thin. An ounce of gold may thus be spread over 100 square feet; 282,000 of such leaves placed upon each other form a pile of only one inch high. These leaves will allow light to pass through them, and always appear green or blue when held up to the light, though they exhibit the ordinary colour of gold by reflected light; extremely thin leaves of gold, obtained by partially dissolving ordinary gold leaf by floating it on solution of cyanide of potassium, transmit a violet or a red light, according to their thickness, though they still appear yellow by reflected light, and if taken up on a glass plate and heated to about 600° F. they lose their golden reflection and become ruby red, changing to green if pressed with a hard substance. If very finely divided gold be suspended in water, it imparts a violet or red colour to it. Such coloured fluids containing very minute particles of gold in a state of suspension, may be obtained by the action of phosphorus dissolved in ether upon a very weak solution of gold in aqua regia; on standing for a long time, the particles of finely divided gold are deposited, having the same tint as that which they previously exhibited when suspended in the liquid; the blue particles being less minute are soonest deposited, but the red particles require many months to settle down. These divers colours of finely divided gold are taken advantage of in painting upon porcelain, and the well-known magnificent ruby red glass owes its colour to the same cause. $\frac{1}{100}$th of a grain of gold is capable of imparting a deep rose colour to a cubic inch of fluid.

The extreme ductility of gold is exemplified in the manufacture of gold thread for embroidery, in which a cylinder of silver having been covered with gold leaf, it is drawn through a wire-drawing plate and reduced to the thinness of a hair; in this way six ounces of gold are drawn into a cylinder two hundred miles in length. Although fusing at about the same temperature as copper, gold is seldom cast, on account of its great contraction during solidification.

Gold is not even affected to the same extent as silver by exposure to the atmosphere, for sulphuretted hydrogen has no action upon it, and hence no metal is so well adapted for coating surfaces which are required to preserve their lustre.

The gold is sometimes applied to the surfaces of metals in the form of an amalgam, the mercury being afterwards driven off by heat. Metals may also be gilt by means of a boiling solution prepared by dissolving gold in aqua regia, and adding an excess of bicarbonate of potash or of soda. But the most elegant process of gilding is that of electro-gilding, in which the object to be gilt is connected with the negative (zinc) end of the galvanic battery, and immersed in a solution of cyanide of gold in cyanide of potassium, in which is also placed a gold plate connected with the positive (copper) end of the battery, and intended, by gradually dissolving, to replace the gold abstracted from the solution at the negative pole.

A gold crucible is very useful in the laboratory for effecting the fusion of substances with caustic alkalies, which would corrode a platinum crucible.

299. *Oxides of gold.*—Two compounds of gold with oxygen have been obtained, Au_2O and Au_2O_3, but neither of them is of any great practical importance.

Sesquioxide of gold or *auric acid* (Au_2O_3) is prepared from the solution of gold in *aqua regia*, by boiling it with excess of potash, decomposing the aurate of potash with sulphuric acid, and purifying the auric acid by dissolving it in nitric acid and precipitating by water. It forms a yellow precipitate, which is easily decomposed by exposure to light or to a temperature of 500° F. By dissolving it in potash and evaporating *in vacuo*, the *aurate of potash* is obtained in yellow needles ($K_2O.Au_2O_3$, 6Aq.). *Suboxide of gold* (Au_2O) forms a dark precipitate when protochloride of gold is decomposed by potash.

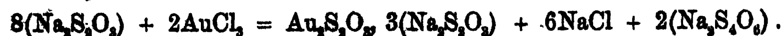
The *chlorides of gold* correspond in composition to the oxides. The *terchloride of gold* ($AuCl_3$) is obtained by dissolving gold in hydrochloric acid with one-fourth of its volume of nitric acid, and evaporating on a water-bath to a small bulk; on cooling, yellow prismatic crystals of a compound of the terchloride with hydrochloric acid ($AuCl_3$.HCl.6Aq.) are deposited, from which the hydrochloric acid may be expelled by a gentle heat (not exceeding 250° F.), when the terchloride forms a red brown deliquescent mass, dissolving very readily in water, giving a bright yellow solution which stains the skin and other organic matter purple when exposed to light, depositing finely divided gold. Almost every substance capable of combining with oxygen reduces the gold to the metallic state. The inside of a perfectly clean flask or tube may be covered with a film of metallic gold by a dilute solution of the terchloride mixed with citric acid and ammonia, and gently heated. The facility with which it deposits metallic gold, and the resistance of the deposited metal to atmospheric action, has rendered terchloride of gold very useful in photography. Alcohol and ether readily dissolve the terchloride, the latter being able to extract it from its aqueous solution. Red crystals of terchloride of gold are sublimed when thin gold foil is gently heated in a current of chlorine. Terchloride of gold (like perchloride of platinum) forms crystallisable compounds with the alkaline chlorides and with the hydrochlorates of organic bases, and affords great help to the chemist in defining these last. *Aurochloride of sodium* forms reddish yellow prismatic crystals ($NaCl.AuCl_3$,4Aq.) which are sometimes sold for photographic purposes.

Protochloride of gold (AuCl) is obtained by gently heating the terchloride, when it fuses and is decomposed at 350° F., leaving the protochloride, which is reduced to metallic gold at about 400° F. The protochloride is sparingly soluble in water and of a pale-yellow colour. Boiling water decomposes it into metallic gold and terchloride.

Fulminating gold is obtained as a buff precipitate when ammonia is added to solution of terchloride of gold; its composition is not well established, but appears to be $Au_2O_3.4NH_3.H_2O$. It explodes violently when gently heated.

The *Sel d'or* of the photographer is a hyposulphite of gold and soda ($Au_2S_2O_3$, $3(Na_2S_2O_3)$, 4Aq.), which is obtained in fine white needles by pouring a solution of one part of terchloride of gold into a solution of

three parts of hyposulphite of soda, and adding alcohol, in which the double salt is insoluble. Its formation may be explained by the equation—

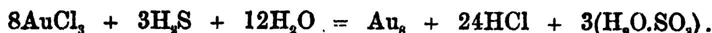


$$8(Na_2S_2O_3) + 2AuCl_3 = Au_2S_2O_3,\ 3(Na_2S_2O_3) + 6NaCl + 2(Na_2S_4O_6).$$

It is doubtful whether the above formula represents the true constitution of this salt, for it is not decomposed by acids in the same manner as ordinary hyposulphites. Nitric acid causes the whole of the gold to separate in the metallic state.

Purple of Cassius, which is employed for imparting a rich red colour to glass and porcelain, is a compound of gold, tin, and oxygen, which are believed to be grouped according to the formula $Au_2O.SnO_2, SnO.SnO_2.4Aq$. It may be prepared by adding protochloride of tin to a mixture of bichloride of tin and terchloride of gold; 7 parts of gold are dissolved in *aqua regia* and mixed with 2 parts of tin also dissolved in *aqua regia*; this solution is largely diluted with water, and a weak solution of 1 part of tin in hydrochloric acid is added, drop by drop, till a fine purple colour is produced. The purple of Cassius remains suspended in water in a very fine state of division, but subsides gradually, especially if some saline solution be added, as a purple powder. The fresh precipitate dissolves in ammonia, but the purple solution is decomposed by exposure to light, becoming blue, and finally colourless, metallic gold being precipitated, and binoxide of tin left in solution.

The *sulphides of gold* are not thoroughly known. When hydrosulphuric acid acts on solution of terchloride of gold, a black precipitate of Au_2S, Au_2S_3 is obtained, which dissolves in alkaline sulphides. The salt $Na_2S, Au_2S, 8Aq.$ has been obtained, in colourless prisms soluble in alcohol. The precipitated sulphide of gold is not dissolved by the acids, with the exception of *aqua regia*. Nitric acid oxidises the sulphur, leaving metallic gold. When hydrosulphuric acid is added to a boiling solution of terchloride of gold, the metal itself is precipitated—



$$8AuCl_3 + 3H_2S + 12H_2O = Au_8 + 24HCl + 3(H_2O.SO_3).$$

A yellowish grey brittle *arsenide of gold* $(AuAs_2)$ has been found in quartz in Australia.

ON SOME OF THE

USEFUL APPLICATIONS OF CHEMICAL PRINCIPLES NOT HITHERTO MENTIONED.

CHEMICAL PRINCIPLES OF THE MANUFACTURE OF GLASS.

300. Glass is defined chemically to be a mixture of two or more silicates, one of which is a silicate of an alkali, the other being a silicate of lime, baryta, oxide of iron, oxide of lead, or oxide of zinc.

If silicic acid be fused with an equal weight of carbonate of potash or soda, a transparent glassy mass is obtained, but this is slowly dissolved by water, and would therefore be incapable of resisting the action of the weather; if a small proportion of lime or baryta, or of the oxides of iron, lead, or zinc, be added, the glass becomes far less easily affected by atmospheric influences.

The most valuable property of glass, after its transparency and permanence, is that of assuming a viscid or plastic consistency when fused, which allows it to be so easily fashioned into the various shapes required for use or ornament.

The composition of glass is varied according to the particular purpose for which it is intended, the materials selected being fused in large clay crucibles placed in reverberatory furnaces, and heated by a coal-fire or in a gas-furnace.

Ordinary *window glass* is essentially composed of silicate of soda and silicate of lime, containing one molecule (13·3 per cent.) of soda, one molecule (12·9 per cent.) of lime, and five molecules (69·1 per cent.) of silicic acid; it also usually contains a little alumina. This variety of glass is manufactured by fusing 100 parts of sand with about 35 parts of chalk and 35 parts of soda-ash: a considerable quantity of broken window glass is always fused up at the same time. Of course, the carbonic acid of the chalk and of the carbonate of soda is expelled in the gaseous state, and in order that this may not cause the contents of the crucible to froth over during the fusion, the materials are first *fritted* together, as it is termed, at a temperature insufficient to liquefy them, when the carbonic acid is evolved gradually, and the fusion afterwards takes place without effervescence.

Occasionally sulphate of soda is employed instead of the carbonate, when it is usual to add a small proportion of charcoal, in order to reduce the sulphuric to the state of sulphurous acid, which is far more easily expelled. Before the glass is worked into sheets, it is allowed to remain

at rest for some time in the fused state, so that the air-bubbles may escape, and the *glass-gall* or scum (consisting chiefly of sulphate of soda and chloride of sodium), which rises to the surface, is removed.

Plate glass is also chiefly a silicate of soda and lime, but it contains, in addition, a considerable quantity of silicate of potash (74 per cent. of silicic acid, 12 of soda, 5·5 of potash, and 5·5 of lime). The purest white sand is selected, and great care is taken to exclude impurities.

Crown glass, used for optical purposes, contains no soda, since that alkali has the property of imparting a greenish tint to glass, which is not the case with potash. This variety of glass, therefore, is prepared by fusing sand with carbonate of potash and chalk in such proportions that the glass may contain one molecule (22 per cent.) of potash, one molecule (12·5 per cent.) of lime, and four molecules (62 per cent.) of silicic acid.

The glass of which *wine bottles* are made is of a much cheaper and commoner description, consisting chiefly of silicate of lime, but containing, in addition, small quantities of the silicates of the alkalies, of alumina, and of oxide of iron, to the last of which it owes its dark colour. It is made of the coarsest materials, such as common red sand (containing iron and alumina), soap-makers' waste (containing lime and small quantities of alkali), refuse lime from the gas-works, clay, and a very small proportion of rock-salt.

Flint glass, which is used for table glass and for ornamental purposes, is a double silicate of potash and oxide of lead, containing one molecule (13·67 per cent.) of potash, one molecule (33·28 per cent.) of oxide of lead, and six molecules (51·93 per cent.) of silicic acid. It is prepared by fusing 300 parts of the purest white sand with 200 parts of minium (red oxide of lead), 100 parts of refined pearl-ash, and 30 parts of nitre. The fusion is effected in crucibles covered in at the top to prevent the access of the flame, which would reduce a portion of the lead to the metallic state. The nitre is added in order to oxidise any accidental impurities which might reduce the lead.

The presence of the oxide of lead in glass very much increases its fusibility, and renders it much softer, so that it may be more easily cut into ornamental forms; it also greatly increases its lustre and beauty.

Baryta has also the effect of increasing the fusibility of glass, and oxide of zinc, like oxide of lead, increases its brilliancy and refracting power, on which account it is employed in some kinds of glass for optical purposes. Glass of this description is also made by substituting boracic acid for a portion of the silicic acid.

Some varieties of glass, if heated nearly to their melting point, and allowed to cool slowly, become converted into an opaque very hard mass resembling porcelain (*Réaumur's porcelain*). This change, which is known as *devitrification*, is due to the crystallisation of the silicates contained in the mass, and by again fusing it, the glass may be restored to its original transparent condition.

In producing *coloured glass*, advantage is taken of its property of dissolving many metallic oxides with production of peculiar colours. It has been mentioned above that bottle glass owes its green colour to the presence of oxide of iron; and since this oxide is generally found in small quantity in sand, and even in chalk, it occasionally happens that a glass which is required to be perfectly colourless turns out to have a slight green tinge. In order to remove this, a small quantity of some oxidising agent

is usually added, in order to convert the oxide of iron into the sesquioxide, which does not impart any colour when present in minute proportion. A little nitre is sometimes added for this purpose, or some arsenious acid, which yields its oxygen to the oxide of iron, and escapes in the form of vapour of arsenic; red oxide of lead (Pb_3O_4) may also be employed, and is reduced to oxide of lead (PbO), which remains in the glass. Binoxide of manganese is often added as an oxidising agent, being reduced to the state of oxide of manganese (MnO), which does not colour the glass; but care is then taken not to add too much of the binoxide, for a very minute quantity of this substance imparts a beautiful amethyst purple colour to glass.

Suboxide of copper is used to produce a red glass, and the finest ruby glass is obtained (as already mentioned at p. 400) by the addition of a little gold. The oxides of antimony impart a yellow colour to glass; a peculiar brown-yellow shade is given by charcoal in a fine state of division, and sesquioxide of uranium produces a fine greenish-yellow glass. Green glass is coloured either by oxide of copper or sesquioxide of chromium, whilst oxide of cobalt gives a magnificent blue colour. For black glass, a mixture of the oxides of cobalt and manganese is employed. The white enamel glass is a flint glass, containing about 10 per cent. of binoxide of tin. Bone ash is also used to impart this appearance to glass.

CHEMISTRY OF THE MANUFACTURE OF POTTERY AND PORCELAIN.

301. The manufacture of pottery obviously belongs to an earlier period of civilisation than that of glass, since the raw material, clay, would at once suggest, by its plastic properties, the possibility of working it into useful vessels, and the application of heat would naturally be had recourse to in order to dry and harden it. Indeed, at the first glance, it would appear that this manufacture, unlike that of glass, did not involve the application of chemical principles, but consisted simply in fashioning the clay by mere mechanical dexterity into the required form. It is found, however, at the outset, that the name of *clay* is applied to a large class of minerals, differing very considerably in composition, and possessing in common the two characteristic features of plasticity and a predominance of silicate of alumina.

It has already been stated (p. 285) that *kaolin* is a hydrated silicate of alumina, and it is from this material that the best variety of porcelain is made. This clay is eminently plastic, and can therefore be readily moulded, but when baked, it shrinks very much, so that the vessels made from it lose their shape and often crack in the kiln. In order to prevent this, the clay is mixed with a certain proportion of sand, chalk, bone-ash, or heavy-spar; but another difficulty is thus introduced, for these substances diminish the tenacity of the clay, and would thus render the vessels brittle. A further addition must therefore be made, of some substance which fuses at the temperature employed in baking the ware, and thus serves as a cement to bind the unfused particles of clay, &c., into a compact mass. Feldspar (silicate of alumina and potash) answers this purpose; or carbonate of potash or of soda is sometimes added, to convert a portion of the silica into a fusible alkaline silicate. With a mixture of clay with sand and feldspar (or some substitutes), a vessel may be moulded which will preserve its shape and tenacity when baked, but it will be

easily pervious to water, and thus quite unfit for ordinary use. It has, therefore, to be water-proofed by the application of some easily fusible material, which shall either form a glaze over the surface, or shall become incorporated with the body of the ware, and the vessel is then fit for all its uses. Handles and ornaments in relief are moulded separately, and fixed on the ware before baking, and coloured designs are transferred from paper to the porous ware before glazing.

The manufacture of *Sèvres porcelain* is one of the most perfect examples of this art. The purest materials are selected in the following proportions:—Kaolin (porcelain clay), 62 parts; chalk, 4 parts; sand, 17 parts; feldspar, 17 parts. These materials are ground up with water before being mixed, and the coarser particles allowed to subside; the creamy fluids containing the finer particles in suspension are then mixed in the proper proportions, and allowed to settle; the paste deposited at the bottom is drained, thoroughly kneaded, and stored away for some months in a damp place, by which its texture is considerably improved, and any organic matter which it contains becomes oxidised and removed; the oxidation being effected partly by the sulphates present, which become reduced to sulphides. It is then moulded into the required forms, and dried by simple exposure to the air. The vessels are packed in cylindrical cases of very refractory clay, which are arranged in a furnace or kiln of peculiar construction, and very gradually but strongly heated by the flame of a wood fire. When sufficiently baked, the *biscuit* porcelain has to be glazed, and great care is taken that the glaze may possess the same expansibility by heat as the ware itself, for otherwise it would crack in all directions as the glazed ware cooled. The glaze employed at Sèvres is a mixture of feldspar and quartz very finely ground, and suspended in water, to which a little vinegar is added to prevent the glaze from subsiding too rapidly. When the porous ware is dipped into this mixture, it absorbs the water, and retains a thin coating of the mixture of quartz and feldspar upon its surface. It is now baked a second time, when the glaze fuses, partly penetrating the ware, partly remaining as a varnish upon the surface.

When the ware is required to have some uniform colour, a mineral pigment capable of resisting very high temperatures is mixed with the glaze; but coloured designs are painted upon the ware after glazing, the ware being then baked a third time, in order to fix the colours. These colours are glasses coloured with metallic oxides, and ground up with oil of turpentine, so that they may be painted in the ordinary way upon the surface of the ware; when the latter is again heated in the kiln, the coloured glass fuses, and thus contracts a firm adhesion with the ware.

Gold is applied either in the form of precipitated metallic gold, or of fulminating gold, being ground up in either case with oil of turpentine, burnt in, and burnished.

English porcelain is made from Cornish clay mixed with ground flints, burnt bones, and sometimes a little carbonate of soda, borax, and binoxide of tin, the last improving the colour of the ware. It is glazed with a mixture of Cornish stone (consisting of quartz and feldspar), flint, chalk, borax, and sometimes white lead to increase its fusibility.

Stone-ware is made from less pure materials, and is covered with a glaze of silicate of soda, in a very simple manner, by a process known as *salt-glazing*. The ware is coated with a thin film of sand by dipping it in a mixture of fine sand and water, and is then intensely heated in a kiln into

which a quantity of damp salt is presently thrown. The joint action of the aqueous vapour and the salt converts the sand into silicate of soda, which fuses into a glass upon the surface of the ware—



$$2NaCl + H_2O + SiO_2 = Na_2O.SiO_2 + 2HCl.$$

Pipkins, and similar earthenware vessels, are made of common clay mixed with a certain proportion of marl and of sand. They are glazed with a mixture of 4 or 5 parts of clay, with 6 or 7 parts of litharge. The colour of this ware is due to the presence of peroxide of iron.

Bricks and tiles are also made from common clay mixed, if necessary, with sand. These are very often grey, or blue, or yellow, before baking, and become red under the action of heat, since the iron, which is originally present as carbonate ($FeO.CO_2$), becomes converted into the red peroxide (Fe_2O_3) by the atmospheric oxygen.

The impure varieties of clay fuse much more easily than pure clay, so that, for the manufacture of the refractory bricks for lining furnaces, of glass-pots, crucibles for making cast steel, &c., a pure clay is employed, to which a certain quantity of broken pots of the same material is added, to prevent the articles from shrinking whilst being dried.

Dinas fire-bricks are made from a peculiar siliceous material found in the Vale of Neath, and containing alumina with about 98 per cent. of silica. The ground rock is mixed with 1 per cent. of lime and a little water before moulding. These bricks are expanded by heat, whilst ordinary fire-bricks contract.

Blue bricks are glazed by sprinkling with *iron scurf*, a mixture of particles of stone and iron produced by the wear of the siliceous grindstones employed in grinding gun-barrels, &c. When the bricks are fired, a glaze of silicate of iron is formed upon them.

CHEMISTRY OF BUILDING MATERIALS.

302. Chemical principles would lead to the selection of pure silica (quartz, rock-crystal) as the most durable of building materials, since it is not acted on by any of the substances likely to be present in the atmosphere; but even if it could be obtained in sufficiently large masses for the purpose, its great hardness presents an obstacle to its being hewn into the required forms. Of the building stones actually employed, *granite*, *basalt*, and *porphyry* are the most lasting, on account of their capability of resisting for a great length of time the action of water and of atmospheric carbonic acid; but their hardness makes them so difficult to work, as to prevent their employment except for the construction of pavements, bridges, &c., where the work is massive and straightforward, and much resistance to wear and tear is required. The *millstone grit* is also a very durable stone, consisting chiefly of silica, and employed for the foundations of houses. *Freestone* is a term applied to any stone which is soft enough to be wrought with hammer and chisel, or cut with a saw; it includes the different varieties of sandstone and limestone. The sandstones consist of grains of sand cemented together by clay or limestone. The *Yorkshire flags* employed for paving are siliceous stones of this description. The *Craigleith sandstone*, which is one of the freestones used in London, contains about 98 per cent. of silica, together with some carbonate of lime.

The building stones in most general use are the different varieties of

carbonate of lime. The durability of these is in proportion to their compact structure; thus *marble*, being the most compact, has been found to resist for many centuries the action of the atmosphere, whilst the more porous limestones are corroded at the surface in a very short time. *Portland stone*, of which St Paul's and Somerset House are built, and *Bath stone*, are among the most durable of these; but they are all slowly corroded by exposure to the atmosphere. The chief cause of this corrosion appears to be the mechanical disintegration caused by the expansion, in freezing, of the water absorbed in the pores of the stone. In order to determine the relative extent to which different stones are liable to be disintegrated by frost, a test has been devised, which consists in soaking the stone repeatedly in a saturated solution of sulphate of soda and allowing it to dry, when the crystallisation of the salt disintegrates the stone, as freezing water would, so that if the particles detached from the surface be collected and weighed, a numerical expression for the resistance of the material will be obtained. *Magnesian limestones* (carbonate of lime with carbonate of magnesia) are much valued for ornamental architecture, on account of the ease with which they may be carved, and are said to be more durable in proportion as they approach the composition expressed by the formula $CaO.CO_2$, $MgO.CO_2$.* The magnesian limestone from Bolsover Moor, of which the Houses of Parliament are built, contains 50 per cent. of carbonate of lime, 40 of carbonate of magnesia, with some silica and alumina.

It is probable that a slow corrosion of the surface of limestone is effected by the carbonic acid continually deposited in aqueous solution from the air; and it is certain that in the atmosphere of towns the limestone is attacked by the sulphuric acid which results from the combustion of coal and the operations of chemical works. The Houses of Parliament have suffered severely, probably from this cause. Many processes have been recommended for the preservation of building stones, such as waterproofing them by the application of oily and resinous substances, and coating or impregnating them with solution of soluble glass and similar matters; but none seems yet to have been thoroughly tested by practical experience.

Purbeck, *Ancaster*, and *Caen stones* are well-known limestones employed for building.

303. The *mortar* employed for building is composed of 1 part of freshly slaked lime and 2 or 3 parts of sand intimately mixed with enough water to form an uniform paste. The hardening of such a composition appears to be due, in the first instance, to the absorption of carbonic acid from the air, by which a portion of the lime is converted into carbonate, and this, uniting with the unaltered hydrate of lime, forms a solid layer adhering closely to the two surfaces of brick or stone, which it cements together. In the course of time the lime would act upon the silica, producing silicate of lime, and this chemical action would render the adhesion more perfect. The chief use of the sand here, as in the manufacture of pottery (p. 405), is to prevent excessive shrinking during the drying of the mortar.

In constructions which are exposed to the action of water, mortars of peculiar composition are employed. These *hydraulic mortars* or *cements*, as they are termed, are prepared by calcining mixtures of carbonate of

* Any excess of carbonate of lime above that required by this formula may be dissolved out by treating the powdered magnesian limestone with weak acetic acid.

lime with from 10 to 30 per cent. of clay, when the carbonic acid is expelled, and the lime combines with a portion of the silicic acid from the clay, producing a silicate of lime, and probably also, with the alumina, to form aluminate of lime. When the calcined mass is ground to powder and mixed with water, the silicates of alumina and lime, and the aluminate of lime, unite to form hydrated double silicates and aluminates, upon which water has no action. Roman cement is prepared by calcining a limestone containing about 20 per cent. of clay, and hardens in a very short time after mixing with water.

For Portland cement (so called from its resembling Portland stone) a mixture of river mud (chiefly clay) and limestone is calcined at a very high temperature.

Concrete is a mixture of hydraulic cement with small gravel. A specimen of this material from a very ancient Phœnician temple was as hard as a rock, and contained nearly 30 per cent. of pebbles.

Scott's cement is prepared by passing air containing a small quantity of sulphurous acid, evolved from burning sulphur, over quick-lime heated to dull redness. The setting of this cement appears due to the presence of a small proportion of sulphate of lime very intimately mixed with the quick-lime. The mixture of these substances yields the cement by a less circuitous process.

GUNPOWDER.

304. Gunpowder is a very intimate mixture of saltpetre (nitre or nitrate of potash), sulphur, and charcoal, which do not act upon each other at the ordinary temperature, but when heated together, arrange themselves into new forms, evolving a very large amount of gas.

In order to manufacture gunpowder capable of producing the greatest possible effect, great attention is requisite to the purity of the ingredients, the process of mixing, and the form ultimately given to the finished powder.

CHEMISTRY OF THE INGREDIENTS OF GUNPOWDER—SALTPETRE.—*Nitrate of potash* (KNO_3 or $K_2O.N_2O_5$), *nitre* or *saltpetre*, is found in some parts of India, especially in Bengal and Oude, where it sometimes appears as a white incrustation on the surface of the soil, and is sometimes mixed with it to some depth. The nitre is extracted from the earth by treating it with water, and the solution is evaporated, at first by the heat of the sun, and afterwards by artificial heat, when the impure crystals are obtained, which are packed in bags and sent to this country as *grough* (or impure) saltpetre. It contains a quantity of extraneous matter varying from 1 to 10 per cent., and consisting of the chlorides of potassium and sodium, sulphates of potash, soda, and lime, vegetable matter from the soil, sand, and moisture. The number representing the weight of impurity present is usually termed the *refraction* of the nitre, in allusion to the old method of estimating it by casting the melted nitre into a cake and examining its fracture, the appearance of which varies according to the amount of foreign matter present.

Peruvian or *Chili saltpetre* is the *nitrate of soda* ($NaNO_3$ or $Na_2O.N_2O_5$) found in Peru and Chili in beds beneath the surface soil. It is often spoken of as *cubical saltpetre*, since it crystallises in rhombohedra, easily mistaken for cubes, whilst *prismatic saltpetre*, nitrate of potash, crystallises in six-sided prisms. Nitrate of soda cannot be substituted for nitrate of potash as an ingredient of gunpowder, since it attracts moisture from the air, becoming

damp, and appears to be less powerful in its oxidising action upon combustible bodies at a high temperature. The Peruvian saltpetre, however, forms a very important source from which to prepare the nitrate of potash for gunpowder, since it is easily converted into this salt by double decomposition with chloride of potassium. The latter salt is now imported in so large a quantity from the salt-mines of Stassfurth (p. 260), that it enables nitrate of soda to be very cheaply converted into nitrate of potash, and renders Indian saltpetre of less importance to the manufacturer of gunpowder.

In order to understand the production of saltpetre by the decomposition of nitrate of soda with chloride of potassium, it is necessary to be acquainted with the solubility of those salts and of the salts produced by their mutual decomposition.

100 parts of boiling water dissolve		100 parts of cold water dissolve	
218	parts of nitrate of soda,	50	parts of nitrate of soda,
53	,, chloride of potassium,	33	,, chloride of potassium,
200	,, nitrate of potash,	30	,, nitrate of potash,
37	,, chloride of sodium.	36	,, chloride of sodium.

It is a general rule that when two salts in solution are mixed, which are capable of forming, by exchange of their metals, a salt which is less soluble in the liquid, that salt will be produced and separated.

Thus when nitrate of soda and chloride of potassium are mixed, and the solution boiled down, chloride of sodium is deposited, and nitrate of potash remains in the boiling liquid—



$$NaNO_3 + KCl = KNO_3 + NaCl.$$

When this is allowed to cool, the greater part of the nitrate of potash crystallises out, leaving the remainder of the chloride of sodium in solution.

The method usually adopted is to add the chloride of potassium by degrees to the boiling solution of nitrate of soda, to remove the chloride of sodium with a perforated ladle in proportion as it is deposited, and, after allowing the liquid to rest for some time to deposit suspended impurities, to run it out into the crystallising pans.

The potash-salt required for the conversion of nitrate of soda into nitrate of potash is sometimes obtained from the refuse of the beet root employed in the manufacture of sugar.

Nitrate of potash is sometimes prepared from the nitrates obtained in the *nitre-heaps*, which consist of accumulations of vegetable and animal refuse with limestone, old mortar, ashes, &c. These heaps are constructed upon an impermeable clay floor under a shed to protect them from rain. One side of the heap is usually vertical and exposed to the prevailing wind, the other side being cut into steps or terraces. They are occasionally moistened with stable drainings, which are allowed to run into grooves cut in the steps at the back of the heap. In such a mass, at an atmospheric temperature between 60° and 70° F., nitrates of the various bases present in the heap are slowly formed, and being dissolved by the moisture, are left by it, as it evaporates on the vertical side, in the form of an efflorescence. When this has accumulated in sufficient quantity, it is scraped off, together with a few inches of the *nitrified* earth, and extracted with water, which dissolves the nitrates, whilst the undissolved earth is built up again on the terraced back of the heap. After two or

three years the heap is entirely broken up and reconstructed. The principal nitrates which are found dissolved in the water are those of potash, lime, magnesia, and ammonia, the three last of which may be converted into nitrate of potash by decomposing them with carbonate of potash.

The formation of nitric acid in these heaps probably results from chemical changes similar to those which occur in the soils in which nitre is naturally formed, but, at present, these changes are not thoroughly explained. Some chemists are of opinion that the nitric acid is formed by the union of atmospheric nitrogen and oxygen, encouraged by the presence of porous solids, and of matters undergoing oxidation. The explanation which is best supported by experimental evidence is that which refers the formation of nitric acid to the oxidation of ammonia (p. 128), evolved by the putrefaction of the nitrogenised matters which the heaps contain, this oxidation also being much promoted by the presence of the strongly alkaline lime, and of the porous materials capable of absorbing ammonia and presenting it under circumstances favourable to oxidation.

In *refining saltpetre* for the manufacture of gunpowder, the impure salt is dissolved in about an equal weight of boiling water in a copper boiler, the solution run through cloth filters to remove insoluble matter, and allowed to crystallise in a shallow wooden trough lined with copper, the bottom of which is formed of two inclined planes (fig. 278). Whilst cooling, the solution is kept in continual agitation with wooden stirrers, in order that the saltpetre may be deposited in the minute crystals known as *saltpetre flour*, and not in the large prisms which are formed when the solution is allowed to crystallise tranquilly, and which contain within them cavities enclosing some of the impure liquor from which the saltpetre has been crystallised. The saltpetre, being so much less soluble in cold than in hot water, is, in great part, deposited as the liquid cools, whilst the chlorides and other impurities being present in small proportion, and not presenting the same disparity in their solubility at different temperatures, are retained in the liquid. The saltpetre flour is drained in a wooden trough with a perforated bottom, and transferred to a washing-cistern, where it is allowed to remain for half an hour in contact with two or three successive small quantities of water, to wash away the adhering impure liquor; it is then allowed to drain thoroughly, and in that state, containing from three to six per cent. of water, according to the season, is ready to be transferred to the incorporating mill or to a hot-air oven, where it is dried if not required for immediate use.

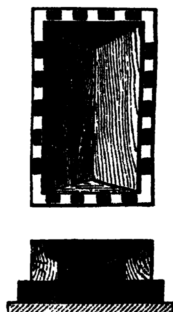


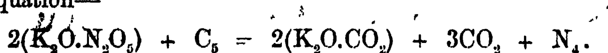
Fig. 278.

The mother-liquor, from which the saltpetre flour has been deposited, is boiled down and crystallised, the crystals being worked up with the next batch of grough nitre. The final washings of the flour are returned to the boiler in which the grough nitre is originally dissolved. When the saltpetre contains very much colouring matter, a little glue or animal charcoal is employed by the refiner to assist in its removal.

The impurities most objectionable in the saltpetre employed for gunpowder would be the chlorides of potassium and sodium, which cause it to absorb moisture easily from the air; the chief test, therefore, to which

the refiner subjects it, is the addition, to its solution in distilled water, of a few drops of solution of nitrate of silver, which causes a milkiness, due to the separation of a precipitate of chloride of silver, if the chlorides have not been entirely removed. Moreover, the sample should dissolve entirely in water, to a perfectly clear colourless solution, which should have no effect on blue or red litmus paper, and should give no cloudiness with chloride of barium (indicating the presence of sulphates), or with oxalate of ammonia (indicating lime), when these are added to separate portions of it. Very minute quantities of sulphates and of lime, such as may have been derived from the use of river water in washing the flour, are generally disregarded.

305. *Properties of saltpetre.*—Nitrate of potash is usually distinguishable by the long striated or grooved six-sided prismatic form in which it crystallises (though it may also be obtained in rhombohedral crystals like those of nitrate of soda), and by the deflagration which it produces when thrown on red-hot coals. It fuses at about 660° F. to a colourless liquid, which solidifies on cooling to a translucent brittle crystalline mass. The *sal prunelle* of the shops consists of nitre which has been fused and cast into balls. At a red heat it effervesces from the escape of bubbles of oxygen, and is converted into nitrite of potash (KNO_2), which is itself decomposed by a higher temperature, evolving nitrogen and oxygen, and leaving a mixture of potash and peroxide of potassium. In contact with any combustible body, it undergoes decomposition with great rapidity, five-sixths of its oxygen being available for the oxidation of the combustible substance, and the nitrogen being evolved in the free state; thus, in contact with carbon, the decomposition of the nitre may be represented by the equation—



$$2(K_2O.N_2O_5) + C_5 = 2(K_2O.CO_2) + 3CO_2 + N_4.$$

Since the combustion of a large quantity of material may be thus effected in a very small space and in a short time, the temperature produced is much higher than that obtained by burning the combustible in the ordinary way. The specific gravity of saltpetre is 2·07, so that one cubic inch weighs 523 grains (obtained by multiplying the weight of a cubic inch of water, 252·5 grains by 2·07). Since 202 grains (2 molecules) of nitre contain 80 grains (5 atoms) of oxygen available for the oxidation of combustible bodies, 523 grains, or one cubic inch, of nitre, would contain 207 grains or 605 cubic inches of available oxygen, a volume which would be contained in about 3000 cubic inches of air; hence, one volume of saltpetre represents, in its power of supporting combustion, 3000 volumes of atmospheric air. It also enables some combustible substances to burn without actual flame, as is exemplified by its use in *touchpaper* or *slow port-fire*, which consists of paper soaked in a weak solution of saltpetre and dried.

If a continuous design be traced on foolscap paper with a brush dipped in a solution of 30 grains of saltpetre in 100 grains of water, and allowed to dry, it will be found that when one part of the pattern is touched with a red-hot iron, it will gradually burn its way out, the other portion of the paper remaining unaffected.

A mixture of 90 grains of saltpetre, 30 of sulphur, and 30 of moderately fine sawdust (*Baumé's flux*) will deflagrate with sufficient intensity to fuse a small silver coin into a globule; the mixture may be pressed down in a walnut shell or a small porcelain crucible, and the coin buried in it, the flame of a lamp being applied outside until deflagration commences.

Pulvis fulminans is a mixture of 3 parts of saltpetre, 1 part of sulphur, and 2 of carbonate of potash, all carefully dried; when it is heated on an iron plate, no action takes place till it begins to melt, when it explodes very violently.

306. CHARCOAL FOR GUNPOWDER.—Charcoal has been already described as the residue of the destructive distillation of wood, in which process the hydrogen and oxygen of the wood are for the most part expelled in the forms of wood naphtha (CH_4O), pyroligneous acid ($C_2H_4O_2$), carbonic acid, carbonic oxide, water, &c., leaving a residue containing a much larger proportion of carbon than the original wood, and therefore capable of producing a much higher temperature (p. 66) by its combustion with the saltpetre. The higher the temperature to which the charcoal is exposed in its preparation, the larger the proportion of hydrogen and oxygen expelled, and the more nearly does the charcoal approach in composition to pure carbon; but it is not found advantageous in practice to employ so high a temperature, since it yields a dense charcoal of difficult combustibility, and therefore less fitted for the manufacture of powder.

The following table exhibits the composition of dried alder-wood and of the charcoal obtained at different temperatures. The incombustible matter or ash of the wood and charcoal is here omitted.

In 100 parts.	Temperature of charring.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Alder-wood, . .	...	48·63	5·94	44·75	0·68
Charcoal, . . .	518° F.	71·0	4·6	24·4	
,,	662°	77·2	4·1	18·7	
,,	800°	82·6	1·9	15·5	
,,	2000°	83·3	2·3	14·4	
,,	2300°	89·2	1·4	9·4	
,,	2700°	95·4	0·7	3·9	
,,	Above 3000°	98·8	0·6	0·6	

This table shows that at temperatures between 800° and 2000° F., there is very little alteration in the composition of the charcoal, and it is within these limits that the charcoal employed for the manfacture of gunpowder in this country is prepared. Between these limits, however, the density and consequent inflammability of the charcoal vary considerably, that prepared at the lower temperatures igniting most readily. Hence it is desirable that the temperature of carbonisation should not exceed an ordinary low red heat (about 1000° F.)

The charcoal prepared between 500° and 600° F. has a brown colour (*charbon roux*), and although it is more easily inflamed than the black charcoal obtained at higher temperatures, the presence of so large a proportion of oxygen so much diminishes its calorific value, that its employment in gunpowder is not advantageous. It is used on the Continent in the manufacture of sporting-powder, and is prepared by exposing the wood, in an iron cylinder, to the action of high-pressure steam heated to about 540° F.

Light woods, such as alder, willow, and dogwood,* are selected for the preparation of charcoal for gunpowder, because they yield a lighter and

* Dogwood charcoal is not made from the true dogwood (*cornus*) but from the alder buckthorn (*Rhamnus frangula*), commonly called black dogwood.

more easily combustible charcoal, dogwood being employed for the best quality of powder for small arms. This wood is chiefly imported, since it has not been successfully grown in this country. The wood is stripped of its bark, and either exposed for a length of time to the air or dried in a hot chamber. Considerable loss of charcoal takes place if damp wood be charred, a portion of the carbon being oxidised by the steam at a high temperature.

In order to convert the wood into charcoal, 1½ cwt. of wood is packed into a sheet iron cylinder or *slip* (fig. 279), one end of which is closed by a tightly fitting cover, and the other by a perforated plate, to allow of the escape of the gases and vapours expelled during the carbonisation. This cylinder is then introduced into a cylindrical cast-iron retort, built into a brick furnace, and provided with a pipe (L) for the escape of the products, which are usually carried back into the furnace (B) to be consumed. The process of charring occupies from 2½ to 3½ hours, and as soon as it is completed, which is known by the violet tint of the (carbonic oxide) flame from the pipe leading into the fire, the slip is transferred to an iron box or *extinguisher*, where the charcoal is allowed to cool. About 40 lbs. of charcoal are obtained from the above quantity of wood. Charcoal prepared by this process is spoken of as *cylinder charcoal*, to distinguish it from *pit charcoal*, prepared by the ordinary process of charcoal-burning described at p. 62, and which is employed for fuze compositions, &c., but not for the best gunpowder. The fitness of the charcoal for the manufacture of powder is generally judged of by its physical characters. It is of course desirable that the charcoal should be as free from incombustible matter as possible. The proportion of the ash left by different charcoals varies considerably, but it seldom exceeds two per cent. This ash consists chiefly of the carbonates of potash and lime; it also contains phosphate of lime, carbonate of magnesia, silicate and sulphate of potash, chloride of sodium, and the oxides of iron and manganese.

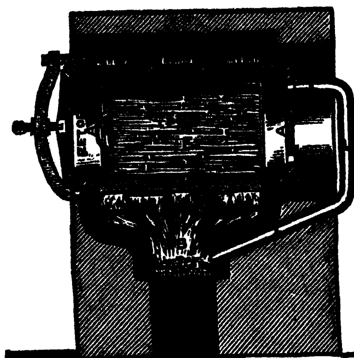


Fig. 279.—Charcoal retort.

The charcoal is kept for about a fortnight before being ground, for if ground when fresh, before it has absorbed moisture from the air, it is liable to spontaneous combustion. The grinding is effected in a mill resembling a coffee-mill, and the charcoal is afterwards sifted.

The properties of charcoal have been already described; its great tendency to absorb moisture from the air is of some importance in the manufacture of gunpowder, from its causing a false estimate to be made of the proportion employed, unless the actual amount of water present in the charcoal is known.

Tar charcoal is the name given to sticks of charcoal which have accidentally become coated with a shining film of carbon left behind by tar which has condensed upon it in the retorts; it is sometimes rejected by the powder manufacturer.

307. SULPHUR FOR GUNPOWDER.—*Distilled sulphur* (p. 189) is the

variety always employed for the manufacture of gunpowder, the *sublimed sulphur* being employed for fuze compositions, &c. The alleged reason for the preference is that the sublimed sulphur, having been deposited in a chamber containing much sulphurous and sulphuric acid vapours, its pores have become charged with acid which would be injurious in the powder; but it has been pointed out (p. 191) that distilled sulphur consists entirely of the soluble or electro-negative variety of sulphur, whilst sublimed sulphur contains a large proportion of the insoluble or positive sulphur, which would probably influence its action in gunpowder. The sulphur should leave scarcely a trace of incombustible matter when burnt, and after stirring the powdered sulphur for some time with warm distilled water, the latter should only very feebly redden blue litmus. As an ingredient of gunpowder, sulphur is valuable on account of the low temperature (560° F.) at which it inflames, thus facilitating the ignition of the powder. Its oxidation by saltpetre appears also to be attended with the production of a higher temperature than is obtained with charcoal, which would have the effect of accelerating the combustion and of increasing, (by expansion,) the volume of gas evolved. The sulphur is ground under edge-runners (fig. 280) and sifted.

The difference in the inflammability of sulphur and charcoal is strikingly shown by heating a square of coarse wire gauze over a flame till it is red-hot in the centre, placing it over a jar of oxygen, allowing it to cool till it no longer kindles charcoal-powder sprinkled through it from a pepper-box, and whilst the cloud of charcoal is still floating in the gas, throwing in sulphur from a second box; the hot gauze will inflame the sulphur, and this will kindle the charcoal.

An iron rod allowed to cool below redness may be used to stir a mixture of charcoal with (3 parts of) nitre; but if dipped into powdered sulphur, at once inflames it, and the flame of the sulphur will kindle the mixture. The effect of the same rod upon mixtures of nitre with charcoal alone, and with charcoal and sulphur, is instructive.

The acceleration of the combustion of gunpowder by the sulphur is well shown by laying a train, of which one-half consists of a mixture of 75 nitre and 25 charcoal, and the other of 75 nitre, 15 charcoal, and 10 sulphur, a red-hot iron being applied at the junction of the two trains to start them together.

308. Manufacture of gunpowder.—The proportions of the ingredients of gunpowder have been varied somewhat in different countries, the saltpetre ranging from 74 to 77 per cent., the charcoal from 12 to 16, and the sulphur from 9 to 12·5 per cent. English Government powder contains 75 per cent. of nitre, 15 per cent. of charcoal, 10 per cent. of sulphur. An extra pound of saltpetre is generally added at Waltham, to compensate for loss in manufacture.

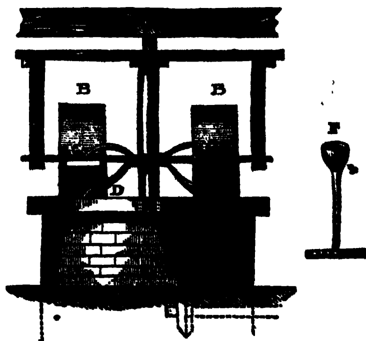


Fig. 280.—Incorporating mill.

The powdered ingredients* are first roughly mixed in a revolving gun-metal drum, with mixing arms turning in an opposite direction, and the mixture is subjected, in quantities of about 50 lbs. at a time, to the action of the *incorporating mill* (fig. 280), where it is sprinkled with water, poured through the funnel (F), or from a

* The amount of water in the moist saltpetre (p. 411) is ascertained by drying and melting a weighed sample before the proportions are weighed out.

can with a fine rose, and exposed to trituration and pressure under two cast-iron edge-runners (B), rolling round in different paths upon a cast-iron bed, a very intimate mixture being thus effected by the same kind of movement as in a common pestle and mortar, the distribution of the nitre through the mass being also assisted by its solubility in water. A wooden scraper (C) tipped with copper, prevents the roller from getting clogged, and a *plough* (D) keeps the mixture in the path. Of course, the water employed to moisten the powder must be as free from deliquescent salts (especially chlorides, see p. 411) as possible; at Waltham condensed steam is employed; the quantity required varies with the state of the atmosphere. The duration of the incorporating process is varied according to the kind of powder required, the slow-burning powder employed for cannon being sufficiently incorporated in about 3 hours, whilst rifle-powder requires 5 hours.

The dark-grey mass of *mill-cake* which is thus produced, contains 2 or 3 per cent. of water. It is broken up by passing between grooved rollers of gun-metal, and is then placed, in layers of about half an inch thick, between copper plates packed in a stout gun-metal box lined inside and outside with wood, in which it is subjected for a quarter of an hour to a pressure of about 70 tons on the square foot, in a hydraulic press, which has the effect of condensing a larger quantity of explosive material into a given volume, and of diminishing the tendency of the powder to absorb moisture from the air and to disintegrate or *dust* after granulation. The *press-cake* thus obtained is very hard and compact, resembling slate in appearance. As far as its chemical nature is concerned, it is finished gunpowder, but if it be reduced to powder and a gun loaded with it, the combustion of the charge is found to take place too slowly to produce its full effect, since the pulverulent form offers so great an obstacle to the passage of the flame by which the combustion is communicated from one end of the charge to the other. The press-cake must, therefore, be *granulated* (*corned*) or broken up into grains of sufficient size to allow the rapid passage of the flame between them, and the consequent immediate firing of the whole charge The granulation is effected by crushing the press cake between successive pairs of toothed gun-metal rollers, from which it falls on to sieves, which separate it into grains of different sizes, the dust, or *meal powder*, passing through the last sieve. At Waltham, the R.L.G. (rifle large grain) passes through a sieve of 4 meshes to the inch, and is retained on one of 8 meshes, whilst the R.F.G. (rifle fine grain) passes through a 12 mesh and is retained on a 20 mesh sieve. The granulated powders are freed from dust by passing them through revolving cylinders of wooden frame-work covered with canvas or wire cloth, and the fine grain powder is glazed by the friction of its own grains against each other in revolving barrels. The large-grain powders are sometimes glazed or *faced* with graphite, by introducing a little of that substance into the glazing-barrels with the powder. The powder is dried in a chamber heated by steam very gradually, so as not to injure the grain, and is once more dusted in canvas cylinders before being packed.

For very large charges, the grains having a diameter of $\frac{1}{4}$ to $\frac{1}{8}$ inch (R.L.G.) are found to burn too rapidly, exerting too great a strain upon the gun. In such cases, *pebble powder*, the grains of which vary from $\frac{5}{8}$ to $\frac{1}{2}$ inch in diameter, is employed. This has been made hitherto by breaking up the slabs of press-cake on wooden tables with mallets armed with bronze points.

Prismatic powder consists of large grains made of a regular six-sided prismatic form by compressing the powder-meal (without previously making it into press-cake) in moulds, with metal punches, whereas the pebble powder is irregular in form. The prismatic powder is made with perforations in the direction of its length, to facilitate the passage of flame through the charge.

Pellet powder is moulded in a similar manner into cylindrical pellets about ½ inch long, and ¾ inch in diameter, perforated at one end to about the centre.

309. Properties of gunpowder.—Good gunpowder is composed of hard angular grains, which do not soil the fingers, and have a perfectly uniform dark-grey colour. Its specific gravity (*absolute density*) as determined by the *densimeter*,* varies between 1·67 and 1·84, and its *apparent density* (obtained by weighing a given measure of the grain against an equal measure of water) varies from 0·89 to 0·94, so that a cubic foot will weigh from 55 to 58 lbs. When exposed to air of average dryness, gunpowder absorbs from 0·5 to 1·0 per cent. of water. In damp air it absorbs a much larger proportion, and becomes deteriorated in consequence of the saltpetre being dissolved, and crystallising upon the surface of the grains. Actual contact with water dissolves the saltpetre and disintegrates the grains. When very gradually heated in air, gunpowder begins to lose sulphur, even at 212° F., this ingredient passing off rapidly as the temperature rises, so that the greater part of it may be expelled without inflaming the powder, especially if the powder is heated in carbonic acid or hydrogen, to prevent contact with air. If gunpowder be suddenly heated to 600° F. in air, it explodes, the sulphur probably inflaming first; but out of contact with air a higher temperature is required to inflame it. The ignition of gunpowder by flame is not ensured unless the flame be flashed among the grains of powder; it often takes some time to ignite powder with the flame of a piece of burning paper or stick, but contact with a red-hot solid body inflames it at once. A heap of good powder, when fired on a sheet of white paper, burns without sparks and without scorching or kindling the paper, which should exhibit only scanty black marks of charcoal after the explosion. If the powder has not been thoroughly incorporated, it will leave minute globules of fused nitre upon the paper. Two ounces of the powder should be capable of throwing a 68-lb. shot to a distance of 260 to 300 feet from an 8-inch mortar at 45° elevation.

This mode of testing powder by the *eprouvette* mortar is not now applied to Government powders. Far more accurate results are obtained by measuring the velocity imparted to a projectile of known weight by a given charge of the powder. The velocity is measured by means of a *chronoscope* which registers the distance travelled by the shot in a given time by causing it to cut the wire of one electrical circuit at the commencement of its flight, and that of another at the conclusion, thus telegraphing its velocity to the instrument room at a distance.

Cannon powder (R.L.G.) is tested by firing a charge of 1 lb. from a muzzle-loader rifled gun, with a 12 lb. shot. Small arm powder (R.F.G.) is fired from a Snider-Enfield or Martini-Henry rifle. The mean velocity at a distance of 105 feet from the muzzle is determined. For R.L.G. it

* This is a simple apparatus for determining the weight of mercury displaced by a given weight of gunpowder from which all the air has been exhausted.

amounts to about 1000 feet per second. A charge of 70 grs. of R.F.G. in the Snider-Enfield rifle gives a velocity somewhat greater than this.

Very fortunately, it is difficult to explode gunpowder by concussion, though it has been found possible to do so, especially on iron, and accidents appear to have been caused in this way by the iron edge-runners in the incorporating mill, when the workmen have neglected the special precautions which are laid down for them. The use of stone upon iron in the incorporation is avoided, because of the great risk of producing sparks, and copper is employed in the various fittings of a powder mill wherever it is possible.

The electric spark is, of course, capable of firing gunpowder, though it is not easy to ensure the inflammation of a charge by a spark unless its conducting power is slightly improved by keeping it a little moist, which may be effected by introducing a minute quantity of chloride of calcium.

310. Products of explosion of gunpowder.—In the explosion of gunpowder, the oxygen of the nitre converts the carbon of the charcoal chiefly into carbonic acid (CO_2), part of which assumes the gaseous state, whilst the remainder combines with the potash of the nitre to form carbonate of potash ($K_2O.CO_2$). The greater part of the sulphur is converted into sulphuric acid (SO_3), which forms sulphate of potash ($K_2O.SO_3$). The chief part of the nitrogen contained in the nitre is evolved in the uncombined state. The rough chemical account of the explosion of gunpowder, therefore, is that the mixture of nitre, sulphur, and charcoal is resolved into a mixture of carbonate of potash, sulphate of potash, carbonic acid, and nitrogen, the two last being gases, the elastic force of which, when expanded by the heat of the combustion, accounts for the mechanical effect of the explosion.

But in addition to these, several other substances are found among the products of the explosion. Thus, the presence of sulphide of potassium (K_2S) may be recognised by the smell of hydrosulphuric acid produced on moistening the solid residue in the barrel of a gun, and hydrosulphuric acid (H_2S) itself may often be perceived in the gases produced by the explosion, the hydrogen being derived from the charcoal. A little marsh-gas (CH_4) is also found among the gases, being produced by the decomposition of the charcoal, a portion of the hydrogen of which is also disengaged in the free state. Carbonic oxide (CO) is always detected among the products. It is evident that the collection for analysis of the products of explosion must be attended with some trouble, and that considerable differences are to be expected between the results obtained by different operators, from the variation of the circumstances under which the powder is fired and the products collected. When the powder is slowly burnt, a considerable proportion of the nitrogen in the saltpetre is evolved in the form of nitric oxide gas (NO), which is not found among the products of the rapid explosion of powder.

Some of the most recent experiments upon the explosion of gunpowder have been made under conditions very similar to those which occur in practice, the powder having been confined in a thin iron case and suspended in the centre of a strong iron globe exhausted of air, in which the powder was fired by electricity, so that the gaseous and solid products of the explosion remained within the globe, and could be submitted to analysis. Two samples of powder were thus examined, but their com-

position differed from that of English Government powder stated above, as will be seen by the following table :—

		I.		II.
Nitre,		73·78	..	77·15
Sulphur,		12·80	...	8·63
Charcoal, viz.,	Carbon,	10·88	...	11·78
	Hydrogen,	0·38	...	0·42
	Oxygen,	1·82	...	1·79
	Ash,	0·31	..	0·28
		99·97		100·05

About 570 grs. of powder were exploded in each experiment. The gas collected was found to be inflammable, as would be expected from the flash which is always perceived at the muzzle when a gun is discharged.

100 grs. of sample I. gave 107·4 cub. in. of gas at 32° F. and 30 in. Bar.
" " II. " 117·5 " " "

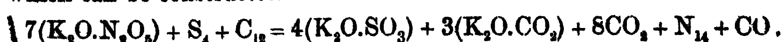
The gases contained, in 100 cubic inches—

	I.		II.
Nitrogen,	37·58		35·33
Carbonic acid (CO_2),	42·74	.	48·90
Carbonic oxide (CO),	10·19		5·18
Hydrogen,	5·93	.	6·90
Sulphuretted hydrogen (H_2S),	0·86		0·67
Marsh-gas (CH_4),	2·70	.	3·02
	100·00		100·00

The products of explosion furnished by 100 grains of each powder, were—

	I.		II.
Sulphate of potash ($K_2O.SO_3$),	36·95	..	36·17
Carbonate of potash ($K_2O.CO_2$),	19·40		20·78
Hyposulphite of potash ($K_2O.S_2O_2$),	2·85		1·77
Sulphide of potassium (K_2S),	0·11		0·00
Sesquicarbonate of ammonia,	2·68		2·66
Charcoal,	2·67		2·60
Sulphur,	4·69		1·16
Nitrogen,	9·77		10·06
Carbonic acid (CO_2),	17·39	.	21·79
Carbonic oxide (CO),	2·64		1·47
Hydrogen,	0·11		0·14
Sulphuretted hydrogen (H_2S),	0·27	..	0·23
Marsh-gas (CH_4),	0·40	.	0·49
	99·33		99·32

In both these cases, it will be seen that if the charcoal and sulphur which took no part in the combustion be left out of consideration, the sulphate and carbonate of potash formed together more than $\frac{8}{9}$ of the solid products of explosion; and that the carbonic acid and nitrogen taken together amounted, in the one case to $\frac{8}{10}$, and in the other to $\frac{16}{19}$ of the gaseous products. If only the chief products of the explosion be taken into consideration, viz., sulphate and carbonate of potash, carbonic acid, carbonic oxide, and nitrogen, the following equation is the simplest which can be constructed from the above numerical data :—



$$7(K_2O.N_2O_5) + S_4 + C_{12} = 4(K_2O.SO_3) + 3(K_2O.CO_2) + 8CO_2 + N_{14} + CO.$$

This equation, however, would represent a gunpowder composed of

Nitre,	83·8
Sulphur,	7·5
Charcoal,	8·5
	99·8

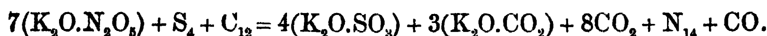
and would require the products of decomposition to be—

Sulphate of potash,	41·2
Carbonate of potash,	24·5
Carbonic acid,	20·8
Nitrogen,	11·6
Carbonic oxide,	1·6
	99·7

Reasoning from analogy with other chemical operations, it seems probable that the explosion of gunpowder really includes a number of chemical changes which cannot be simply represented in one equation, and that whilst the above equation, or some similar one, represents the principal reaction which takes place during the explosion, there are other minor reactions in progress, the products of which are found in smaller quantity.

311. CALCULATION OF THE FORCE OF FIRED GUNPOWDER.—The mechanical force exerted in the explosion of gunpowder depends upon the production of a large volume of gas from a small volume of solid, the volume of the gas being increased by the expansive effect of the heat generated in the combustion of the charcoal and sulphur. To calculate the amount of this mechanical force, it is necessary to ascertain the volume of gas which would be evolved by a given volume of powder, and the extent to which this gas would be expanded by the heat at the instant of explosion.

In order to illustrate this calculation, let it be assumed that the equation given above correctly represents the explosion of the powder, viz.—



$$7(K_2O.N_2O_5) + S_4 + C_{12} = 4(K_2O.SO_3) + 3(K_2O.CO_2) + 8CO_2 + N_{14} + CO.$$

Now, it is calculated from the Table of Atomic Weights that

$7(K_2O.N_2O_5)$	(202 × 7)	=	1414 grains.
S_4	(32 × 4)	=	128 ,,
C_{12}	(12 × 12)	=	144 ,,
Gunpowder,			1686 ,,

			At 60° F., and 30 in. Bar.
$8CO_2$	(44 × 8)	= 352 grains	= 744·0 cub. inches.
14N	(14 × 14)	= 196 ,,	= 650·8 ,,
CO		= 28 ,,	= 93·0 ,,
			1487·8 ,,

Hence it appears that 1686 grains of gunpowder would yield 1487·8 cubic inches of gas measured at 60° F. and 30 in. barometric pressure.

If one cubic foot of the powder weighs 58 lbs., one cubic inch will weigh 234·9 grains, and will evolve 207 cubic inches of gas measured at 60° F. and 30 in. Bar.*

But the mechanical force exerted by the powder depends upon the volume of this gas at the period of explosion, and in order to calculate this, we must ascertain what would be its temperature at that period.

A carefully conducted experiment has shown that the explosion of one part by weight of gunpowder is able to raise the temperature of 619·5

* It will be remembered that this is only the apparent density of the powder, as obtained by the old method of weighing a cubic foot of the loose powder. The density of a rammed down charge would of course be greater than this.

parts by weight of water from 0° C. to 1° C., or to raise the temperature of one part by weight of water from 0° C. to 619°·5 C., supposing the water to be capable of bearing so great an elevation of temperature without change of state.

This result is generally expressed by saying that the combustion of the powder evolves 619·5 *units of heat* (the unit of heat being the quantity required to raise 1 part by weight of water from 0° C. to 1° C.)

But the products of the explosion of powder will be raised to a higher temperature than 619°·5 C., because their specific heat is lower than that of water.

For the purpose of this calculation, the specific heat of a substance may be defined as the quantity of heat required to raise 1 gr. of the substance through 1° of the thermometer, water being taken as the unit.

It is evident that if the specific heat of each product of the explosion be multiplied by the actual weight of that product, the result will be the quantity of heat required to raise that product 1° in temperature.

The specific heats of the products have been ascertained by experiment, and are contained in the first column of figures in the following table. The actual weight of each product from the explosion of 1 gr. of powder is contained in the second column, and the third column shows the quantity of heat required to raise each product 1° C. (representing as unity the quantity of heat required to raise 1 gr. of water from 0° C. to 1° C.)

	Spec. Heat.		From 1 gr. powder.		
Sulphate of potash, . .	0·1901	×	0·412	=	0·07832
Carbonate of potash, .	0·2162	×	0·246	=	0·05319
Carbonic acid, . .	0·2164	×	0·209	=	0·04523
Nitrogen, . . .	0·2440	×	0·116	=	0·02830
Carbonic oxide, . .	0·2479	×	0·017	=	0·00421
					0·20925

The quantity of heat, therefore, which is required to raise, through 1° C., the joint products of the explosion of one grain of gunpowder is 0·20925 of the above-mentioned unit.

Dividing the 619·5 units of heat generated in the explosion, by the quantity of heat required to raise the joint products through one degree, viz., 0·20925, we obtain 2960° C. (= 5328° F.) for the number of degrees through which the products will be raised by the explosion, *i.e.*, for the temperature of the products at the moment of explosion.*

It remains to be ascertained what volume would be occupied, at 5328° F., by the 207 cubic inches of gas at 60° F. evolved from one cubic inch of powder.

The expansion which gases suffer when heated amounts to $\frac{1}{491}$ of their volume at 32° F. for each degree Fahrenheit.

Thus 491 volumes of gas at 32° F. become
492 „ „ 33° F.,

and, if heated 28° above 32°, *i.e.*, to 60° F., they would become 491 + 28, or 519 volumes. If the 491 volumes be heated to 5328° F., or 5296° above 32°, they will expand to 491 + 5296, or 5787 volumes.

The volume of the gas at the moment of explosion, therefore, will be ascertained from the following proportion—

* Strictly speaking, 32° F. should be added, on account of the different positions of the zero in the two scales, but it would not materially affect the result.

Vols. at 60° F.		Vols. at 5328° F.		Cub. in. at 60° F.		Cub. in. at 5328° F.
519	:	5787	: :	207	:	2308

from which it appears that one cubic inch of powder would evolve a quantity of gas measuring 2308 cubic inches at the moment of explosion.

Since the pressure exerted by gases upon the sides of a containing space is inversely as their volume, the gas evolved from a cubic inch of powder, if developed in a space exactly filled by the powder, would exert a pressure of 2308 atmospheres, or 34,620 lbs., or 15½ tons upon the square inch.

It is here supposed, of course, that the whole of the gas is evolved at once, and is immediately raised to the same temperature, conditions never fulfilled in the use of gunpowder in small arms or in cannon, where the combustion of the charge is not instantaneous, but rapidly progressive, where the confining space is rapidly enlarged by the movement of the projectile long before the whole of the charge has exploded, and where the heated gas is cooled by contact with the metal of the piece.

The calculation given above can be regarded only as an illustration of the method, as there are several circumstances which vitiate the conclusion arrived at. The chemical equation on which it is based is confessedly imperfect.

We know little or nothing of the real condition of the products at the moment of the explosion; it is probably very different from that after cooling, when we examine them. From what is known of the effect of heat upon carbonic acid and carbonic oxide, it is almost certain that these gases are at least partially resolved into their elements at the moment of explosion, and it is scarcely likely that the complex molecules of sulphate and carbonate of potash would exist at so high a temperature. Any breaking up of the molecules of carbonic acid, sulphate and carbonate of potash, would increase the expansion, and render the above estimate of the force of fired powder too low.

Again, the specific heats have been stated on the supposition that the gases were perfectly unconfined, whereas in the circumstances under which powder is fired, their expansion is opposed by the projectile. The subjoined table shows that the specific heats of the gases, when restrained from expanding, are much lower :—

Specific Heats.

	At constant pressure and varying volume (unconfined).	At varying pressure and constant volume (confined).
N	0·2440	0·1717
CO	0·2479	0·1753
CO_2	0·2164	0·1702

Any diminution in the specific heats of the products would obviously increase the temperature at the moment of explosion, and therefore the force of the fired powder.

The actual rate of expansion of gases at so high a temperature is inferred from our experience of their behaviour at comparatively low temperatures, and there are some indications of a want of agreement under the two conditions.

The experiments of Andrews have shown that, even at a pressure of 100 atmospheres, carbonic acid exhibits striking deviations from the law that the pressure exerted by a gas is inversely as its volume.

Noble's experiments, made upon a similar plan to those of Karolyi (p. 418), but with much larger charges of powder, and in a vessel provided with a *crusher gauge*, which registers the pressure at the moment of explosion by the compression of a soft copper cylinder, indicate the highest pressure of fired powder in a closed space, as about 40 tons per square inch.

In criticising all attempts to determine the pressure caused by an explosion, it must be remembered that the effects of a given pressure are very different when gradually and when suddenly applied, the same amount of force which produces little effect as a *push*, may act very destructively as a *blow*.

The period over which the combustion of a given weight of powder extends will, of course, depend upon the extent of surface over which it

can be kindled; thus a single fragment of powder weighing 10 grains, even if it were instantaneously kindled over its entire surface, could not evolve so much gas in a given time as if it had been broken into ten separate grains, each of which was kindled at the same instant, since the inside of the large fragment can only be kindled from the outside. Upon this principle a given weight of powder in large grains will occupy a longer period in its explosion than the same weight in small grains, so that the large grain powder is best fitted for ordnance, where the ball is very heavy, and the time occupied in moving it will permit the whole of the charge to be fired before the ball has left the muzzle, whilst in small arms with light projectiles, a finer grained and more quickly burning charge is required. If the fine grain powder were used in cannon, the whole of the gas might be evolved before the containing space had been sensibly enlarged by the movement of the heavy projectile, and the gun would be subjected to an unnecessary strain; on the other hand, a large grain powder, in a musket, would evolve its gas so slowly that the ball might be expelled with little velocity by the first half of it, and the remainder would be wasted. There is good reason to believe that even under the most favourable circumstances, a large proportion of every charge of powder is discharged unexploded from the muzzle of the gun, and is therefore wasted. In blasting rocks and other mining operations, the space within which the powder is confined is absolutely incapable of enlargement until the gas evolved by the combustion has attained sufficient pressure to do the whole work, that is, to rend the rock, for example, asunder. Accordingly, a slowly burning charge will produce the effect, since the rock must give way when the gas attains a certain pressure, whether that happens in one second or in ten. Indeed, a slowly burning charge is advantageous, as being less liable to shatter the rock or coal, and bringing it away in larger masses with less danger. Nitrate of baryta and nitrate of soda are sometimes substituted for a part of the nitrate of potash in mining powder, its combustion being thus retarded.

The same charge of the same powder produces very different results when heated in different ways. If 5 grs. of gunpowder be placed in a wide test-tube, and fired by passing a heated wire into the tube, a slight puff only is perceived; but if the same amount of powder be heated in the tube by a spirit lamp, it will explode with a loud report, and perhaps shatter the tube (a copper or brass tube is safer). In the first case, the combustion is propagated slowly from the particle first touched by the wire; in the second, all the particles are raised at once to pretty nearly the same temperature, and as soon as one explodes, all the rest follow instantaneously.

When gunpowder is slowly burnt, the products of its decomposition are different from those mentioned above; thus, nitric oxide (NO), arising from incomplete decomposition of the nitre, is perceived in considerable quantity, and may be recognised by the red colour produced when it is brought in contact with air.

The white smoke resulting from the explosion of gunpowder consists chiefly of the sulphate and carbonate of potash in a very finely divided state; it seems probable that at the instant of explosion they are converted into vapour, and are afterwards deposited in a state of minute division as the temperature falls. The *fouling* or actual solid residue in the gun is very trifling when the powder is dry and has been well incorporated; a damp or slowly burning powder leaves, as might be expected, a larger residue. The residue always becomes wet on exposure to air, from the great attraction for moisture possessed by the carbonate of potash and sulphide of potassium.

When 10 grains of Waltham Abbey gunpowder are fired in a strong air-tight cylinder, about an inch high, and half an inch in diameter, by the galvanic battery, the interior of the cavity is covered with a snow-white powder composed of sulphate and carbonate of potash, which deliquesces rapidly in a damp atmosphere. No nitric oxide is found in the gas formed by the explosion.

312. *Effect of variations of atmospheric pressure on the combustion of gunpowder.*—From the circumstance that the combustion of gunpowder is independent of any supply of oxygen from the air, it might be supposed that it would be as easily inflamed *in vacuo* as under ordinary atmospheric pressure. This is not found to be the case, however, for a mechanical reason, viz., that the flame from the particles which are first ignited escapes so rapidly into the vacuous space, that it does not inflame the more remote particles. For a similar reason, charges of powder in fuzes are found to burn more slowly under diminished atmospheric pressure, the flame (or heated gas) escaping more rapidly and igniting less of the remaining charge in a given time. It has been determined that if a fuze be charged so as to burn for thirty seconds under ordinary atmospheric pressure (30 inches barometer), each diminution of one inch in barometric pressure will cause a delay of one second in the combustion of the charge, so that the fuze will burn for thirty-one seconds when the barometer stands at 29 inches.

The manufacture of gunpowder may be illustrated by the following experiments on a small scale:—

Preparation of the ingredients—Charcoal.—A few small pieces of wood are placed in a clay crucible, which is then filled up with dry sand and heated in a moderate fire as long as any vapours are evolved, when it may be set aside to cool.

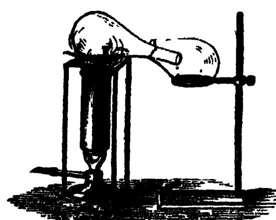


Fig. 281.—Distillation of sulphur.

Sulphur.—500 grains of roll sulphur may be distilled in a Florence flask, using another flask, the neck of which has been cut off (fig. 281), for a receiver, from which the sulphur is afterwards poured, in a melted state, upon a piece of tin-plate.

Nitre.—1000 grains of impure nitre are dissolved, at a moderate heat, in four measured ounces of distilled water, in an evaporating dish (fig. 282); the solution is filtered into a beaker which is placed in cold water, and stirred with a glass rod until it is quite cold. The saltpetre flour thus obtained is collected upon a filter, thoroughly drained, the filter removed from the funnel, spread out, the saltpetre transferred to another piece of filter paper, and pressed between the paper to remove as much of the liquid as possible; it is then spread out on paper and dried on a hot brick. (For the mode of testing its purity see p. 412.)

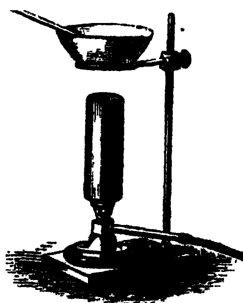


Fig. 282.

Mixture of the ingredients.—60 grains of the charcoal, reduced to a very fine powder, 40 grains of the sulphur, also previously powdered, and 300 grains of the dried nitre, are very intimately mixed in a mortar; 50 grains of the mixture are set aside for comparison. To the remainder enough water is added to make it into a stiff cake, which is well incorporated under the pestle for some time. It is then scraped out of the mortar and allowed to dry slowly at a very gentle heat. When perfectly dry it is crumbled to a coarse powder, and the dust sifted out through a piece of wire gauze. It will be found instructive to compare, in trains and otherwise, the firing of the powder in grains, of the dust, and of the mixed ingredients without incorporation, observing especially the difference in rapidity of burning and in the amount of residue.

CHEMISTRY OF FUEL.

313. Several of the applications of chemical principles in the combustion of fuel have been already explained and illustrated. The object of this chapter is to compare the chemical composition of the most important varieties of fuel, and to exemplify the principles upon which their heating power may be calculated from the results furnished by the analysis of the fuel.

All the varieties of ordinary fuel, of course, contain a large proportion of carbon, always accompanied by hydrogen and oxygen, and sometimes by small proportions of nitrogen and sulphur. Certain mineral substances are also contained in all solid fuels, and compose the ash when the fuel is burnt.

For all practical purposes it may be stated, that the amount of heat generated by the combustion of a given weight of fuel depends upon the weights of carbon and hydrogen, respectively, which enter into combination with the oxygen of the air in the act of combustion of the fuel.

It has been ascertained by experiment that 1 grain of carbon (in the form in which it exists in wood charcoal), when combining with oxygen to form carbonic acid, produces a quantity of heat which is capable of raising 8080 grains of water from 0° to 1° of the centigrade thermometer. This is usually expressed by saying that the *calorific value of carbon* is 8080, or that carbon produces 8080 *units of heat* during its combustion to carbonic acid. If the fuel, therefore, consisted of pure carbon, it would merely be necessary to multiply its weight by 8080 to ascertain its calorific value.

1 grain of hydrogen, during its conversion into water by combustion, evolves enough heat to raise 34,400 grains of water from 0° C. to 1° C., so that the *calorific value of hydrogen* is 34,400.

If the fuel consisted of carbon and hydrogen only, its calorific value would be calculated by multiplying the weight of the carbon in one grain of the fuel by 8080, and that of the hydrogen by 34,400, when the sum of the products would represent the calorific value. But if the fuel contains oxygen already combined with it, the calorific value will be diminished, since this oxygen will consume a part of the combustible without generating heat, because it already exists in a state of combination with the carbon and hydrogen of the fuel. For example, 1 grain of wood contains 0·5 grain of carbon, 0·06 of hydrogen, and 0·44 of oxygen. Now, oxygen combines with one-eighth of its weight of hydrogen to form water, so that the 0·44 grain of oxygen will convert $\cdot 44 \div 8 = \cdot 055$ of the hydrogen into water, without evolution of available heat, leaving only 0·005 available for the production of heat. The calorific value of the wood, therefore, would be represented by the sum of $0{\cdot}005 \times 34{,}400$ ($= 172$) and $0{\cdot}5 \times 8080$ ($= 4040$), which would amount to 4212; or 1 grain of wood should raise 4212 grains of water from 0° C. to 1° C.

These considerations lead to the following *general formula for calculating the calorific value of a fuel* containing carbon, hydrogen, and oxygen, where c, h, and o respectively represent the carbon, hydrogen, and oxygen in one grain of fuel.

The calorific value (or number of grains of water which might be heated

by the fuel from 0° C. to 1° C.) = $8080\,c + 34{,}400\left(h - \frac{o}{8}\right)$ or

$8080\,c + 34{,}400\,h - 4300\,o$.

The calorific value of a fuel, as determined by experiment, is generally less than would be calculated from its chemical composition, in consequence of the absorption of a certain amount of heat attending the chemical decomposition of the fuel. In the case of compounds of carbon and hydrogen, it has been observed that even when they have the same composition in 100 parts, they have not of necessity the same calorific value, the latter being affected by the difference in the arrangement of the component particles of the compound, which causes a difference in the quantity of heat absorbed during its decomposition. Thus olefiant gas (C_2H_4) and cetylene ($C_{16}H_{32}$) have the same percentage composition, and their calculated calorific values would be identical, but the former is found to produce 11,858 units of heat, and the latter only 11,055. As a general rule, however, it is found that the calorific values of the hydrocarbons which contain a multiple of CH_2, agree more nearly with the calculated numbers than do those of hydrocarbons which belong to the marsh-gas series.

It must be remembered that the calorific value of a fuel represents the actual amount of heat which a given weight of it is capable of producing, and is quite independent of the manner in which the fuel is burnt. Thus, a hundredweight of coal will produce precisely the same amount of heat in an ordinary grate as in a wind-furnace, though in the former case the fire will scarcely be capable of melting copper, and in the latter it will melt steel. The difference resides in the *temperature* or *calorific intensity* of the two fires; in the wind-furnace, through which a rapid draught of air is maintained by a chimney, a much greater weight of atmospheric oxygen is brought into contact with the fuel in a given time, so that, *in that time*, a greater weight of fuel will be consumed and more heat will be produced; hence the fire will have a higher temperature, for the temperature represents, not the quantity of heat present in a given mass of matter, but the intensity, or extent to which that heat is accumulated at any particular point. In the case of the wind-furnace here cited, a further advantage is gained from the circumstance, that the rapid draught of air allows a given weight of fuel to be consumed in a smaller space, and, of course, the smaller the area over which a given quantity of heat is distributed, the higher the temperature within that area (as exemplified in the use of the common burning-glass). In some of the practical applications of fuel, such as heating steam-boilers and warming buildings, it is the *calorific value* of the fuel which chiefly concerns us, but the case is different where metals are to be melted, or chemical changes to be brought about by the application of a very high temperature, for it is then the *calorific intensity*, or actual temperature of the burning mass, which has to be considered. No trustworthy method has yet been devised for determining by direct experiment the calorific intensity of fuel, and it is therefore ascertained by calculation from the calorific value.

Let it be required to calculate the calorific intensity, or actual temperature, of carbon burning in pure oxygen gas.

12 grains of carbon combine with 32 grains of oxygen, producing 44 grains of carbonic acid; hence 1 grain of carbon combines with 2·67 grains of oxygen, producing 3·67 grains of carbonic acid. It has been seen above that 1 grain of carbon evolves 8080 units of heat, or is capable

of raising 8080 grains of water from 0° to 1° C., or, on the supposition that the water would bear such an elevation of temperature, the 1 grain of carbon would raise 1 grain of water from 0° to 8080° C. If the *specific heat* (or heat required to raise 1 grain through 1°, see p. 421) of carbonic acid were the same as that of water, 8080° divided by 3·67 would represent the temperature to which the 3·67 grains of carbonic acid would be raised, and therefore the temperature to which the solid carbon producing it would be raised in the act of combustion. But the specific heat of carbonic acid gas is only 0·2163, so that a given amount of heat would raise 1 grain of carbonic acid to nearly five times as high a temperature as that to which it would raise 1 grain of water.

Dividing the 8080 units of heat (available for raising the temperature of the carbonic acid) by 0·2163, the quantity of heat required to raise 1 grain of carbonic acid 1°, we obtain 37,355 for the number of degrees through which 1 grain of carbonic acid might be raised by the combustion of 1 grain of carbon. But there are 3·67 grains of carbonic acid formed in the combustion, so that the above number of degrees must be divided by 3·67 in order to obtain the actual temperature of the carbonic acid at the instant of its production, that is, the temperature of the burning mass. The calorific intensity of carbon burning in pure oxygen is, therefore, (37,355° C. ÷ 3·67 =) 10,178° C. or 18,352° F. But if the carbon be burnt in air, the temperature will be far lower, because the nitrogen of the air will absorb a part of the heat, to which it contributes nothing. The 2·67 grains of oxygen required to burn 1 grain of carbon would be mixed, in air, with 8·93 grains of nitrogen, so that the 8080 units of heat would be distributed over 3·67 grains of carbonic acid and 8·93 grains of nitrogen. Since the specific heat of carbonic acid is 0·2163, the product of 3·67 × 0·2163 (or 0·794) represents the quantity of heat required to raise the 3·67 grains of carbonic acid from 0° to 1° C.

The specific heat of nitrogen is 0·2438; hence 8·93 × 0·2438 (or 2·177) represents the quantity of heat required to raise the 8·93 grains of atmospheric nitrogen from 0° to 1° C.

Adding together these products, we find that 0·794 + 2·177 = 2·971 represents the quantity of heat required to raise both the nitrogen and carbonic acid from 0° to 1° C.

Dividing the 8080° by 2·971, we obtain 2720° C. (4928° F.) for the number of degrees through which these gases would be raised in the combustion, *i.e.*, for the calorific intensity of carbon burning in air. By heating the air before it enters the furnace (as in the hot-blast iron furnace), of course the calorific intensity would be increased; thus if the air be introduced into the furnace at a temperature of 600° F., it might be stated, without serious error, that the temperature producible in the furnace would be 5528° F. (4928° + 600°). The temperature might be further increased by diminishing the area of combustion, as by employing very compact fuel and increasing the pressure of the blast

In calculating the calorific intensity of hydrogen burning in air, from its calorific value, it must be remembered that in the experimental determination of the latter number, the steam produced in the combustion was condensed to the liquid form, so that its latent heat was added to the number representing the calorific value of the hydrogen; but the latent heat of the steam must be *deducted* in calculating the calorific intensity, because the steam goes off from the burning mass and carries its latent heat with it.

1 grain of hydrogen, burning in air, combines with 8 grains of oxygen, producing 9 grains of steam, leaving 26·77 grains of atmospheric nitrogen, and evolving 34,400 units of heat.

It has been experimentally determined that the latent heat of steam is 537° C., that is, 1 grain of water, in becoming steam, absorbs 537 units of heat (or as much heat as would raise 537 grains of water from 0° to 1° C.) without rising in temperature as indicated by the thermometer. The 9 grains of water produced by the combustion of 1 grain of hydrogen will absorb, or render latent, $537 \times 9 = 4833$ units of heat. Deducting this quantity from the 34,400 units evolved in the combustion of 1 grain of hydrogen, there remain 29,567 units of heat available for raising the temperature of the 9 grains of steam and 26·77 grains of atmospheric nitrogen. The specific heat of steam being 0·480, the number $(0{\cdot}480 \times 9 =)$ 4·32 represents the quantity of heat required to raise the 9 grains of steam through 1° C.; and the specific heat of nitrogen (0·2438) multiplied by its weight (26·77 grains), gives 6·53 units of heat required to raise the 26·77 grains of nitrogen through 1° C. By dividing the available heat (29,567 units) by the joint quantities required to raise the steam and nitrogen through 1° C. $(4{\cdot}32 + 6{\cdot}53 = 10{\cdot}85)$, we obtain the number 2725° C. (4937° F.) for the calorific intensity of hydrogen burning in air.

The method of calculating the calorific intensity of a fuel composed of carbon, hydrogen, and oxygen, will now be easily followed.

Let c and h respectively represent the weights of carbon and hydrogen in 1 gr. of fuel, and o that of the oxygen. Then $\frac{o}{8}$ = weight of hydrogen required to convert the oxygen into water, and $h - \frac{o}{8}$ represents the hydrogen which is available for the production of heat. $8080\,c + 34{,}400\left(h - \frac{o}{8}\right)$ represents the calorific value in °C., $= 8080\,c + 34{,}400\,h - 4300\,o$.

$2{\cdot}67\,c$ = atmospheric oxygen consumed by the carbon;

$8\left(h - \frac{o}{8}\right)$ or $8\,h - o$ = atmospheric oxygen consumed by the hydrogen available as fuel.

$3{\cdot}34\,(2{\cdot}67\,c + 8\,h - o)$ = atmospheric nitrogen $= 8{\cdot}92\,c + 26{\cdot}72\,h - 3{\cdot}34\,o$.

Multiplying this by the specific heat of nitrogen 0·2438, we obtain—

$2{\cdot}17\,c + 6{\cdot}51\,h - 0{\cdot}81\,o$ for the heat required to raise the nitrogen through 1° C.

$0{\cdot}794\,c$ represents the quantity of heat required to raise the carbonic acid through 1° C., and $4{\cdot}32\,h$ is the heat required to raise the steam through 1°. Accordingly, the available heat, $8080\,c + 34{,}400\,h - 4300\,o$, must be divided by $0{\cdot}794\,c + 4{\cdot}32\,h + (2{\cdot}17\,c + 6{\cdot}51\,h - 0{\cdot}81\,o)$, or $2{\cdot}96\,c + 10{\cdot}83\,h - 0{\cdot}81\,o$ in order to obtain the calorific intensity.

Hence, the calorific intensity, in centigrade degrees, of a fuel composed of carbon, hydrogen, and oxygen, is represented by the formula—

$$\frac{8080\,c + 34{,}400\,h - 4300\,o}{2{\cdot}96\,c + 10{\cdot}83\,h - 0{\cdot}81\,o.}$$

The actual calorific intensity of the fuel is not so high as it should be according to theory, because a part of the carbon and hydrogen is converted into gas by destructive distillation of the fuel, and this gas is not actually burnt *in the fire*, so that its calorific intensity is not added to that of the burning solid mass. Again, a portion of the carbon is con-

verted into carbonic oxide (CO), especially if the supply of air be imperfect, and much less heat is produced than if the carbon were converted into carbonic acid; although it is true that this carbonic oxide may be consumed above the fire by supplying air to it, the heat thus produced does not increase the calorific intensity or temperature of the fire itself.

One grain of carbon furnishes 2·33 grains of carbonic oxide. These 2·33 grains of carbonic oxide evolve, in their combustion, 5599 units of heat. But if the 1 grain of carbon had been converted at once into carbonic acid, it would have evolved 8080 units of heat, so that 8080 – 5599, or 2481, represents the heat evolved during the conversion of 1 grain of carbon into carbonic oxide, showing that a considerable loss of heat *in the fire* is caused by an imperfect supply of air. It has been already pointed out, in the section relating to Coal, that the formation of carbonic oxide is sometimes encouraged with a view to the production of a flame from non-flaming coal, such as anthracite.

The following table exhibits the average percentage composition of the principal varieties of fuel (exclusive of ash), together with their calculated calorific values and intensities.

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Sulphur.	Calorific Value.	Calorific Intensity.
Wood (Oak), .	50·18	6·08	43·74	...	...	4212° C.	2380° C
Peat, ...	61·53	5·64	32·82	...	...	5654	2547
Lignite (Bovey),	67·86	5·75	23·39	0·57	2·41	6569	2628
Bituminous coal,	79·38	5·34	13·01	1·85	0·39	7544	2694
Charcoal, . . .	90·44	2·91	6·63	...	...	8003	2760
Anthracite, . .	91·86	3·33	3·02	0·84	0·92	8337	2779
Coke, ...	97·32	0·49		2·17		8009	2761

In all ordinary fires and furnaces, a large amount of heat is wasted in the current of heated products of combustion escaping from the chimney. Of course, a portion of this heat is necessary in order to produce the draught of the chimney. In boiler furnaces it is found that, for this purpose, the temperature of the air escaping from the chimney must not be lower than from 500° to 600° F. If the fuel could be consumed by supplying only so much air as contains the requisite quantity of oxygen, a great saving might be effected, but in practice, about twice the calculated quantity of air must be supplied, in order to effect the removal of the products of combustion with sufficient rapidity.

Much economy of fuel may be expected from the use of furnaces constructed on the principle of Siemens' *regenerative furnace*, in which the waste heat of the products of combustion is absorbed by a quantity of fire-bricks, and employed to heat the air before it enters the furnace, two chambers of fire-bricks doing duty alternately, for absorbing the heat from the issuing gas, and for imparting heat to the entering air, the current being reversed by a valve as soon as the fire-bricks are strongly heated.

(For the principles of smoke prevention, and other particulars of the chemistry of fuel, see Coal.)

ORGANIC CHEMISTRY.

314. Although it is impossible to propose a definition of the term *organic substance* which shall not be applicable to some of the substances commonly regarded as *inorganic*, it is found advantageous for the purposes of study to treat *organic chemistry* as a separate division of the science, dealing especially with those substances which are usually obtained, either directly or indirectly, from animals and vegetables.

One very important distinction between organic and inorganic substances is, that the former are for the most part composed of carbon, hydrogen, nitrogen, and oxygen, in different proportions and in various modes of arrangement, and that they are, therefore, much more frequently convertible into each other by metamorphosis, without extraneous addition of matter, than inorganic substances are.

It has been already pointed out that the chemist is gradually learning to produce, though by somewhat clumsy and circuitous processes, many of the substances which were formerly believed incapable of being formed, except through the intervention of life; but no substance possessing an *organised structure*, such as woody fibre or muscular fibre, and no absolutely indispensable organic constituent of animal or vegetable frames, has yet been artificially procured.

It will not escape notice that the four elements which compose the greater number of organic substances, viz., hydrogen, oxygen, nitrogen, and carbon, are, respectively, monatomic, diatomic, triatomic, and tetratomic elements (p. 158), and are, therefore, capable of forming a greater variety of compounds than would be the case if they were elements of equal atomicities.

In the following pages, no strictly scientific classification of organic substances has been adopted, since it would often render it necessary to describe, in separate sections, substances which are, in nature, closely connected with each other, but an empirical arrangement has been followed, so that the reader may find his memory assisted and the interest of the subject sustained, by being enabled to bring the facts and explanations into immediate connection with familiar processes of ordinary life.*

One of the most conspicuous substances standing upon the boundary between organic and inorganic chemistry is the compound of carbon and nitrogen known as *cyanogen*, which is intimately connected with inorganic substances through some of the processes for its production, and through its similarity to the chlorine group of elements, whilst the origin and

* The number of organic substances known to the chemist is so great that a mere list of them would occupy a volume. In the present work a selection has been made of those which are interesting for their practical applications or instructive from theoretical considerations.

chemical properties of a large number of its compounds give them a claim to be ranked among organic substances. The study of this substance, therefore, will form a fit introduction to organic chemistry.

CYANOGEN AND ITS COMPOUNDS.

315. In the beginning of the last century, a manufacturer of colours at Berlin accidentally obtained a blue powder when precipitating sulphate of iron with potash. This substance was used as a colour, under the name of *Prussian blue*, for several years, before any explanation of its production was attempted, or even before the conditions under which it was formed were exactly determined. In 1724 it was shown that Prussian blue could be prepared by calcining dried animal matters with carbonate of potash, and mixing the aqueous solution of the calcined mass, first with sulphate of iron and afterwards with hydrochloric acid; but the most important step towards the determination of its composition was made by Macquer, who found that by boiling it with an alkali, Prussian blue was decomposed, yielding a residue of red oxide of iron, and a solution which reproduced the blue when mixed with a salt of iron, from which he inferred that the colour was a compound of the oxide of iron with an acid for which the alkali had a more powerful attraction,—a belief confirmed, in 1782, by Scheele's observations, that when an alkaline solution prepared for making the blue was exposed to the air, or to the action of carbonic acid, it lost the power of furnishing the colour, but the escaping vapour struck a blue on paper impregnated with oxide of iron. Scheele also prepared this acid in a pure state, and it soon after obtained the name of *prussic acid*.

In 1787 Berthollet found prussic acid to be composed of carbon, hydrogen, and nitrogen, but he also showed that the power of the alkaline liquor to produce Prussian blue depended upon the presence of a yellow salt crystallising in octahedra, and containing prussic acid, potash, and oxide of iron, though the latter was so intimately bound up with the other constituents, that it could not be separated by those substances which are usually employed to precipitate iron.

Porrett, in 1814, applying the greatly increased resources of chemistry to the investigation of this subject, decomposed Prussian blue with baryta, and subsequently removed the baryta from the salt thus obtained by means of sulphuric acid, when he obtained a solution of the acid, which he named *ferruretted chyazic acid*.

In 1815, Gay-Lussac, having boiled Prussian blue (or prussiate of iron, as it was then called) with red oxide of mercury and water, and crystallised the so-called prussiate of mercury, exposed it, in the dry state, to the action of heat, and obtained a gas, having the composition CN, which was called *cyanogen*,* in allusion to its connection with Prussian blue. It was then seen that the substance which had been called ferruretted chyazic acid contained iron and the elements of cyanogen, whence it was called *ferrocyanic acid*, and its salts were spoken of as ferrocyanates. Robiquet first obtained this acid in the crystallised state, having the composition $C_6H_4N_6Fe$; and since it was found that, when brought in contact with metallic oxides, it exchanged the H_4 for an equivalent quantity of the metal, according to the equation—



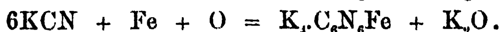
$$H_4.C_6N_6Fe + 2M''O = M_2''.C_6N_6Fe + 2H_2O,$$

* From κυάνεος, blue.

it was concluded that the C_6N_6Fe composed a distinct group or radical, which was named *ferrocyanogen*, the acid being called *hydroferrocyanic acid*, and the salts *ferrocyanides*.

316. *Prussiate of potash.*—The yellow prussiate of potash or *ferrocyanide of potassium* ($K_4C_6N_6Fe.3Aq.$) is manufactured upon a large scale by a process which is the more interesting because it turns to account some of the commonest kinds of refuse, such as old leather, hoof parings, blood, and, in short, any animal matter rich in nitrogen, and not applicable to any more economical purpose. Sometimes these substances are first subjected to destructive distillation for the carbonate of ammonia which they are capable of yielding, and the residual highly nitrogenised charcoal is then used for the production of the ferrocyanide of potassium. Such matters are fused in an iron vessel with carbonate of potash and iron filings, and the fused mass is heated with water in open boilers, when a yellow solution is obtained, which, after evaporation, deposits truncated pyramidal crystals of ferrocyanide of potassium, containing 3 molecules of water.

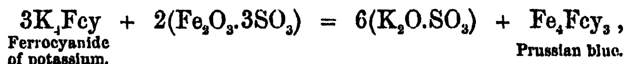
The theory of this process has been elucidated by the researches of Liebig. If carbonate of potash be strongly heated in contact with pure carbon, there result (page 259) carbonic oxide and potassium, $K_2O.CO_2 + C_2 = 3CO + K_2$; but if the carbon be associated with nitrogen, the reduction will be effected at a much lower temperature, and the potassium will combine with an atom of carbon and an atom of nitrogen, to form the *cyanide of potassium* (KCN). When this salt, dissolved in water, is heated with metallic iron in the presence of air, oxygen is absorbed, and the iron dissolved to form ferrocyanide of potassium—



$$6KCN + Fe + O = K_4.C_6N_6Fe + K_2O.$$

The oxygen may also be acquired from the water, an equivalent quantity of hydrogen being evolved.

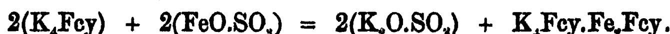
Prussian blue.—For the preparation of Prussian blue it is usual to mix solutions of ferrocyanide of potassium and persulphate of iron, when the blue is precipitated, having been produced according to the equation—



$$\underset{\text{Ferrocyanide of potassium.}}{3K_4Fcy} + 2(Fe_2O_3.3SO_3) = 6(K_2O.SO_3) + \underset{\text{Prussian blue.}}{Fe_4Fcy_3},$$

in which the symbol Fcy represents the group C_6N_6Fe (*ferrocyanogen*), which is capable of playing the same part in many decompositions as if it were an elementary substance. This compound radical has never yet been obtained in the separate state, but it can be traced through a complete series of compounds, in which it exactly resembles chlorine in its chemical relations; thus the *hydroferrocyanic acid* (H_4Fcy), and the ferrocyanides of the metals, are perfectly analogous to hydrochloric acid and the chlorides, though containing a compound radical instead of a simple one; but whereas chlorine is a monatomic radical, combining only with 1 atom of hydrogen, ferrocyanogen is tetratomic; and hence Prussian blue, the *sesquiferrocyanide of iron*, has the composition $Fe_4'''Fcy_3^{iv}$, whilst the sesquichloride is $Fe_2'''Cl_6'$. When Prussian blue is prepared by pouring solution of persulphate of iron into an excess of ferrocyanide of potassium, it is found that, as soon as the excess of the latter has been washed away, the precipitate dissolves in pure water, forming what is used by dyers under the name of *soluble Prussian blue*. Oxalic acid is capable of dissolving the blue, and this solution forms the basis of ordinary blue ink.

Prussian blue is sometimes prepared with the green protosulphate of iron ($FeO.SO_3$), but in that case it is necessary to expose the precipitate for some time to the air, since the first result is a nearly white precipitate which may be regarded as a double ferrocyanide of iron and potassium (K_4Fcy, Fe_2Fcy).



$$2(K_4Fcy) + 2(FeO.SO_3) = 2(K_2O.SO_3) + K_2Fcy.Fe_2Fcy.$$

When this precipitate is exposed to the air, it gradually acquires a dark-blue colour, becoming eventually converted into Prussian blue by oxidation—

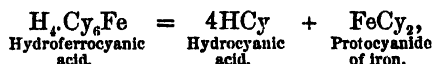


$$3(K_2Fcy.Fe_2Fcy) + O_3 = 3K_4Fcy + Fe_2O_3 + Fe_4Fcy_3.$$

Prussian blue is easily decomposed by alkalies, a brown residue of sesquioxide of iron being left, $Fe_4Fcy_3 + 12KHO = 3K_4Fcy + 2Fe_2O_3 + 6H_2O$. This decomposition is turned to account by the calico-printer for producing a buff or white pattern upon a blue ground. The stuff having been dyed blue by passing, first through a solution of a per-salt of iron, and afterwards through one of ferrocyanide of potassium, the pattern is discharged by an alkali, which leaves the brown peroxide of iron capable of being removed by a dilute acid, when the stuff has been rinsed, so as to leave the design white.

Hydroferrocyanic acid.—By decomposing a cold saturated solution of the ferrocyanide of potassium with about an equal volume of hydrochloric acid, colourless crystals of *hydroferrocyanic acid* (H_4Fcy) are obtained, which are insoluble in hydrochloric acid, but readily soluble in water. When a solution of this acid is heated, it evolves hydrocyanic acid (HCN), and deposits a white precipitate of cyanide of iron $Fe(CN)_2$ which becomes blue on exposure to the air, being converted into Prussian blue; the simplest way of explaining this, as well as many other decompositions of hydroferrocyanic acid and the ferrocyanides, is to view the radical ferrocyanogen as formed by the union of six molecules of cyanogen (CN) and one atom of iron, when hydroferrocyanic acid becomes $H_4.Cy_6Fe$, and Prussian blue $Fe_4.3Cy_6Fe$.*

The decomposition of the hydroferrocyanic acid by heat would then be represented by the equation—



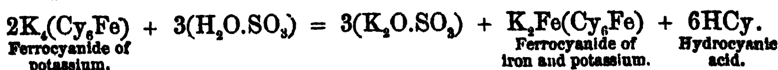
$$\underset{\text{Hydroferrocyanic acid.}}{H_4.Cy_6Fe} = \underset{\text{Hydrocyanic acid.}}{4HCy} + \underset{\text{Protocyanide of iron.}}{FeCy_2},$$

and the formation of Prussian blue from this last compound on exposure to air—



$$9FeCy_2 + O_3 = \underset{\text{Prussian blue.}}{Fe_4.3Cy_6Fe} + Fe_2O_3.$$

Hydrocyanic or *prussic acid.*—Advantage is taken of the decomposition of the ferrocyanide of potassium by acids, in the preparation of solution of hydrocyanic acid for medicinal use. For this purpose, 2 parts of the ferrocyanide of potassium in powder are distilled with $1\frac{1}{2}$ parts of oil of vitriol diluted with 2 parts of water, the vapour of hydrocyanic acid being carefully condensed (see fig. 47). The change is represented by the equation—



$$\underset{\text{Ferrocyanide of potassium.}}{2K_4(Cy_6Fe)} + 3(H_2O.SO_3) = 3(K_2O.SO_3) + \underset{\text{Ferrocyanide of iron and potassium.}}{K_2Fe(Cy_6Fe)} + \underset{\text{Hydrocyanic acid.}}{6HCy}.$$

* Since Cy' is monatomic, $Cy_6'Fe''$ should be tetratomic.

There is left in the retort a pale greenish salt, which rapidly becomes blue when exposed to the air, and is probably identical with the double ferrocyanide of potassium and iron produced when protosulphate of iron is decomposed by ferrocyanide of potassium (p. 433).

The solution of hydrocyanic acid thus obtained is colourless, and exhales the remarkable odour of the acid; its acid characters are very feeble indeed, even more so than those of carbonic acid, but it is extremely poisonous, a very small dose destroying life almost immediately. Hydrocyanic acid is found in laurel-water, and in water distilled from the kernels of many stone-fruits, such as the peach, apricot, and plum. In minute doses hydrocyanic acid is a very valuable remedy, and is employed in medicine in solutions of different strengths. One of these, which is known as the acid of the London Pharmacopœia, contains 2 per cent. of hydrocyanic acid, and is prepared by the process mentioned above. *Scheele's acid* varies in strength, but usually contains between 4 and 5 per cent. of true hydrocyanic acid. This acid is prepared from Prussian blue, by the process originally employed by Scheele when the acid was discovered. It consists in boiling Prussian blue with water and red oxide of mercury, until the blue colour disappears; peroxide of iron is separated, and cyanide of mercury ($HgCy_2$) passes into solution; the latter is filtered, mixed with diluted sulphuric acid, and shaken with iron-filings, which precipitate the mercury in the metallic state, leaving free hydrocyanic acid in the liquid, which is then distilled—



$$HgCy_2 + Fe + H_2O.SO_3 = 2HCy + FeO.SO_3 + Hg.$$

In order clearly to understand this process, it must be known that the mercury exhibits a special tendency to combine with cyanogen, which is sufficiently powerful, in this instance, to bring about the decomposition of the ferrocyanogen existing in the Prussian blue, a part of the cyanogen being exchanged for the oxygen of the oxide of mercury.

It is from the *cyanide of mercury* that the pure anhydrous hydrocyanic acid and cyanogen itself are prepared. For these purposes, it may be obtained by dissolving the red oxide of mercury in hydrocyanic acid, when a double decomposition takes place, exactly as with hydrochloric acid, $HgO + 2HCy = HgCy_2 + H_2O$, and the cyanide of mercury is obtained in square prismatic crystals on evaporating the solution. If these crystals be dried and gently warmed with strong hydrochloric acid, chloride of mercury will be formed, and hydrocyanic acid evolved, $HgCy_2 + 2HCl = HgCl_2 + 2HCy$. The mixed vapours of hydrochloric and hydrocyanic acid are passed over fragments of marble ($CaO.CO_2$), which absorb the hydrochloric acid ($CaO.CO_2 + 2HCl = CaCl_2 + H_2O + CO_2$), but not the hydrocyanic, since the latter is too weak an acid even to displace carbonic acid. The mixture of hydrocyanic and carbonic acids is passed over chloride of calcium to remove aqueous vapour, and afterwards through a tube cooled in a mixture of ice and salt, when the hydrocyanic acid is condensed to a colourless liquid, which evaporates so rapidly when exposed to the air that it lowers the temperature to the freezing point of the acid, which is about 0° F.; at a little above the ordinary temperature (79° F.) it boils, and emits a vapour which burns with a blue flame. When kept for some time it is liable to undergo a spontaneous decomposition, evolving ammonia, and being converted into a brown mass of uncertain composition. The aqueous solution of the acid suffers a similar change, and since exposure to light favours the

decomposition, the medicinal acid is usually kept in bottles covered with paper. The presence of a very small quantity of sulphuric acid prevents this change, and hence the acid prepared by distilling ferrocyanide of potassium with sulphuric acid, which usually contains traces of the latter, can be preserved much better than that prepared by other methods.

When hydriodic acid gas is passed into anhydrous hydrocyanic acid cooled by ice, a crystalline body is formed, which has the composition HCN.HI. It is readily soluble in water and alcohol, but not in ether, and may be sublimed with little decomposition. This substance is not acid, and does not answer to the tests for hydrocyanic acid. When decomposed by potash, it gives ammonia, formiate of potash, and iodide of potassium, so that it may be regarded as the hydriodate of an ammonia formed by the substitution of one molecule of the triatomic radical formyle (CH) for the three atoms of hydrogen; or *hydriodate of formylamine* $N(CH)'''.HI$.

317. *Cyanogen* itself (CN) can be prepared by the mere action of heat upon the cyanide of mercury (in a test-tube provided with a glass jet for burning the gas, fig. 283). This salt resolves itself into metallic mercury cyanogen, and a brown substance which has been called *paracyanogen* (C_3N_3), and appears to have been formed by the union of three molecules of cyanogen. Cyanogen gas is easily distinguished from all others by its peculiar odour and its property of burning with a fine peach-coloured flame. Being nearly twice as heavy as air (sp. gr. 1·8), it may be collected by downward displacement, for water dissolves about four times its volume of the gas, yielding a solution which is prone to undergo a spontaneous decomposition remarkable for the comparatively complex products which it furnishes, amongst which we trace the oxalate $(NH_4)_2C_2O_4$ and formiate (NH_4CHO_2) of ammonia, and urea (CH_4NO), all derived, be it remembered, from the elements of cyanogen and water. In its chemical relations, cyanogen presents a striking resemblance to chlorine. Thus, at a slightly elevated temperature, potassium and sodium take fire in it, forming the cyanides of those metals, precisely as the chlorides would be formed. Again, when cyanogen is absorbed by a solution of potash, the cyanide of potassium and cyanate of potash are formed—

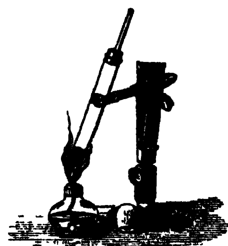
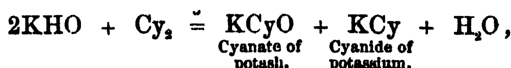


Fig. 283.



$$2KHO + Cy_2 = \underset{\text{Cyanate of potash.}}{KCyO} + \underset{\text{Cyanide of potassium.}}{KCy} + H_2O,$$

just as the chloride of potassium and hypochlorite of potash result from the action of chlorine upon potash, $2KHO + Cl_2 = KClO + KCl + H_2O$. A pressure of about 4 atmospheres is required to liquefy cyanogen, when it forms a colourless liquid of sp. gr. 0·87, freezing to a crystalline mass at − 30° F.

Cyanide of potassium.—The most useful of the cyanides is the cyanide of potassium, which is extensively employed in electro-plating and gilding. This salt may be formed by a very interesting process, which is one of the few in which the atmospheric nitrogen takes part, and consists in passing air over red-hot charcoal which has been previously soaked in a strong solution of carbonate of potash and dried, when the nitrogen requi-

site for the formation of the cyanide is absorbed from the air, and carbonic oxide is disengaged—



$$K_2O.CO_2 + C_4 + N_2 = 2KCN \text{ (Cyanide of potassium)} + 3CO.$$

It is probably by a similar change that the cyanide of potassium is produced in the blast-furnaces (page 302) in which iron ores are reduced, the potash being derived from the ash of the fuel. The cyanide is always prepared for use from the ferrocyanide, which is resolved by a very high temperature into cyanide of potassium and carbide of iron, with evolution of nitrogen.



$$K_4Cy_6Fe \text{ (Ferrocyanide of potassium)} = 4KCy \text{ (Cyanide of potassium)} + FeC_2 + N_2.$$

In order to avoid the loss of the two molecules of cyanogen, it is usual to fuse the ferrocyanide with carbonate of potash in the proportion of 3 parts of the dry carbonate to 7 parts of the dried ferrocyanide; the mixture is fused in a covered earthen crucible, and occasionally stirred until gas ceases to be evolved; the crucible is then removed from the fire, allowed to stand for a minute or two that the metallic iron may subside, and the clear fused cyanide poured out on to a stone. The change involved in this process is represented by the following equation—



$$K_4Cy_6Fe + K_2O.CO_2 = 5KCy + \underset{\text{Cyanate of potash.}}{KCyO} + Fe + CO_2,$$

whence it will be seen that the commercial cyanide of potassium is contaminated with cyanate of potash. It also contains a considerable quantity of carbonate of potash, so that the proportion of cyanide is often only 60 per cent. The white porcelain-like masses of cyanide of potassium deliquesce when exposed to the air, and emit the odour of hydrocyanic acid as well as that of ammonia; the former is disengaged from the cyanide by the action of the atmospheric carbonic acid, whilst the ammoniacal odour is due to the carbonate of ammonia produced by the action of moisture upon the cyanate of potash—



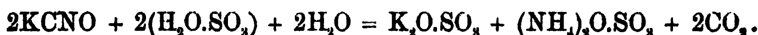
$$\underset{\text{Cyanate of potash.}}{2KCNO} + 4H_2O = K_2O.CO_2 + (NH_4)_2O.CO_2.$$

Pure cyanide of potassium is deposited in colourless cubical crystals when vapour of hydrocyanic acid is passed into an alcoholic solution of potash, or it may be obtained by boiling the commercial cyanide with alcohol and filtering while hot, when the cyanide crystallises out as the solution cools.

The use of cyanide of potassium in electro-plating and gilding depends upon the power of a solution of the salt to dissolve the cyanides of gold and silver, forming compounds which are easily decomposed by the galvanic current, with deposition of metallic gold or silver upon any object capable of conducting the current, which may be attached to the negative pole (p. 361). Solution of cyanide of potassium is also able to dissolve metallic silver and sulphide of silver, which is taken advantage of in removing photographic stains from the hands, and in cleaning silver or gold lace.

At a high temperature, cyanide of potassium is a very powerful reducing agent, abstracting an atom of oxygen from most of the metallic oxides, so as to liberate the metals, being itself converted into cyanate of potash. Thus, when the binoxide of tin is fused with cyanide of potas-

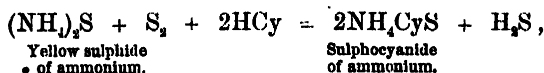
sium, $SnO_2 + 2KCy = Sn + 2KCyO$. This property of the cyanide is often applied in chemical experiments. The cyanate of potash is readily distinguished by the peculiar pungent odour of cyanic acid, which it emits when treated with dilute sulphuric acid, though the greater part of the cyanic acid is decomposed with effervescence, yielding sulphate of ammonia and carbonic acid—



$$2KCNO + 2(H_2O.SO_3) + 2H_2O = K_2O.SO_3 + (NH_4)_2O.SO_3 + 2CO_2.$$

When fused cyanate of potash is triturated with dried oxalic acid, and the mass treated with water, a white insoluble substance is left, which has been called *cyamelide*, and has the composition CHNO, being *metameric* with hydrated cyanic acid, HCNO; when this substance is distilled, hydrated cyanic acid passes over as a colourless liquid, which can only be preserved at a very low temperature, for if the receiver containing it be removed from the freezing mixture employed to condense the cyanic acid, the latter becomes hot and turbid, soon begins to boil violently, and is converted into a white mass of cyamelide resembling porcelain.

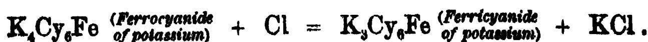
Cyanide of potassium when fused with sulphur, forms a compound corresponding to cyanate of potash, but containing sulphur in place of oxygen, and having the formula KCyS, which is commonly spoken of as *sulphocyanide of potassium*, being represented as containing a compound radical, *sulphocyanogen* CyS = Scy. The sulphocyanide of potassium is generally prepared by fusing 3 parts of dried ferrocyanide of potassium and 1 part of carbonate of potash (the materials for making cyanide of potassium) with 2 parts of sulphur, in a covered crucible. By washing the cooled mass with boiling water, the sulphocyanide is extracted, and may be obtained by evaporating the solution, in prismatic crystals resembling nitre. By decomposing the sulphocyanide of potassium with acetate of lead, the sulphocyanide of lead ($Pb(CyS)_2$) is obtained, and this, when acted upon with sulphuretted hydrogen, yields sulphide of lead and *hydrosulphocyanic acid*, HCyS, the latter being a colourless oily liquid which may be crystallised by cold. This acid is remarkable for the dark red colour (due to sulphocyanide of iron) which it gives with the per-salts of iron, for which sulphocyanide of potassium is frequently employed as a test. A very delicate test (Liebig's test) for hydrocyanic acid, in cases of poisoning, is also founded upon that circumstance, for if a watch-glass moistened with yellow sulphide of ammonium (p. 271) be exposed to the action of vapour of hydrocyanic acid, the latter is absorbed and converted into sulphocyanide of ammonium—



$$\underset{\text{Yellow sulphide of ammonium.}}{(NH_4)_2S} + S_2 + 2HCy = \underset{\text{Sulphocyanide of ammonium.}}{2NH_4CyS} + H_2S,$$

by applying a gentle heat to the watch-glass, any excess of sulphide of ammonium is volatilised, and a drop of perchloride of iron will then give the blood-red colour with the sulphocyanide.

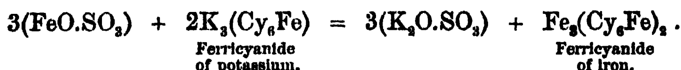
318. *Ferricyanide of potassium.*—When chlorine is passed into a solution of ferrocyanide of potassium, the liquid assumes a brown colour, and, when evaporated, deposits beautiful red rhombic prisms, which are found, on analysis, to have the composition K_3Cy_6Fe, having been formed from the ferrocyanide according to the equation—



$$K_4Cy_6Fe \ (\textit{Ferrocyanide of potassium}) + Cl = K_3Cy_6Fe \ (\textit{Ferricyanide of potassium}) + KCl.$$

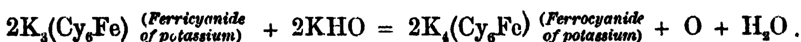
This salt is known as *red prussiate of potash*, or ferricyanide of potassium, and is used in dyeing; for if a piece of stuff be heated in a solution of the ferricyanide acidulated with acetic acid, a blue compound similar to Prussian blue is deposited in the fibre.

Ferricyanide of potassium is also employed for the preparation of *Turnbull's blue* (ferricyanide of iron), which is precipitated when a solution of that salt is mixed with one of sulphate of iron.



$$3(FeO.SO_3) + \underset{\text{Ferricyanide of potassium.}}{2K_3(Cy_6Fe)} = 3(K_2O.SO_3) + \underset{\text{Ferricyanide of iron.}}{Fe_3(Cy_6Fe)_2}.$$

In calico-printing, a mixture of the ferricyanide of potassium with potash is employed as a discharge for indigo, such a mixture acting as a powerful bleaching agent, in consequence of its tendency to impart oxygen to any substance in need of that element, the ferricyanide being converted into the ferrocyanide; thus—



$$2K_3(Cy_6Fe)\ \left(\textit{Ferricyanide of potassium}\right) + 2KHO = 2K_4(Cy_6Fe)\ \left(\textit{Ferrocyanide of potassium}\right) + O + H_2O.$$

The ferricyanide of potassium is assumed to contain a compound radical *ferricyanogen* (Cy_6Fe), which differs from ferrocyanogen in containing triatomic iron Fe''', instead of diatomic iron, Fe''. The formula $Cy_6'Fe'''$ shows that this radical must be triatomic, and not tetratomic like $Cy_6'Fe''$. The *hydroferricyanic acid* (H_3Cy_6Fe) can be obtained in a crystallised state, and many of the corresponding ferricyanides have been examined.

Ferrocyanogen and ferricyanogen are not the only compound radicals of this description; there are *cobalticyanogen* (Cy_6Co), *manganicyanogen* (Cy_6Mn), *chromicyanogen* (Cy_6Cr), *platinocyanogen* (Cy_4Pt), *palladiocyanogen* (Cy_4Pd), and *iridiocyanogen* (Cy_6Ir), but none of these have received any useful applications. The platinocyanides are remarkable for their brilliant colours.

319. *Chlorides of cyanogen.*—When moist cyanide of mercury is shaken up in a bottle of chlorine gas, and set aside for some time in a dark place, the yellow colour of the chlorine disappears, and the bottle is filled with a colourless gas having a remarkably pungent and tear-exciting odour; this is the *gaseous chloride of cyanogen* (CyCl); $HgCy_2 + Cl_4 = HgCl_2 + 2CyCl$. If light have access during this experiment, an oily *liquid chloride of cyanogen*, Cy_2Cl_2, is produced.

The chloride of cyanogen gas may be liquefied by a pressure of four atmospheres, and if the liquid is kept for some days in a sealed tube, it is converted into a white mass of *solid chloride of cyanogen*, Cy_3Cl_3. When this is acted on by water, it yields *cyanuric acid*, $H_3Cy_3O_3$, according to the equation $Cy_3Cl_3 + 3H_2O = 3HCl + H_3Cy_3O_3$. This acid is very interesting on account of its polymeric relation to cyanic acid (HCyO), which may be obtained from it by distillation. It is a tribasic acid, and forms, like tribasic phosphoric acid (p. 233), three series of salts, having the formulæ, respectively, $M'Cy_3O_3$, $M_2'HCy_3O_3$, $M'H_2Cy_3O_3$.

The *cyanide of phosphorus*, PCy_3, has been sublimed in tabular crystals from a mixture of cyanide of silver and terchloride of phosphorus heated in a sealed tube to 280° F. for some hours, and afterwards distilled in a current of dry carbonic acid. Cyanide of phosphorus inflames at a very

low temperature, and is decomposed by water, yielding cyanic and phosphorous acids.

320. *Nitroprussides.*—When ferrocyanide of potassium is boiled with dilute nitric acid, a point is attained at which the solution gives a slate-coloured precipitate with a per-salt of iron; if it be then boiled with an excess of carbonate of soda, filtered, and evaporated, it deposits ruby-red prismatic crystals of *nitroprusside of sodium* ($Na_4Cy_{10}N_2O_3Fe_2.4Aq.$), from which the nitroprussides of other metals may be obtained.

The *hydronitroprussic acid* ($H_4Cy_{10}N_2O_3Fe_2.2Aq,$) has also been prepared and crystallised.

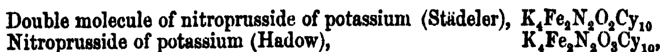
The nitroprussides were found by Hadow to be formed from a double molecule of the ferricyanides by the exchange of two molecules of cyanogen for a molecule of nitrous acid (N_2O_3), and the simultaneous removal of two atoms of the metal with which the ferricyanogen was combined. Thus the double molecule of ferricyanide of potassium, $K_6.Cy_{12}Fe_2$, becomes nitroprusside of potassium, $K_4, Cy_{10}N_2O_3Fe_2$, when boiled with nitric acid, other products being formed at the same time by the oxidising action of the nitric acid.

Based upon this view of its constitution, a more certain and economical process for the production of nitroprusside of sodium was devised by Hadow, which consists in acting upon the ferricyanide of potassium with nitrite of soda, acetic acid, and bichloride of mercury (corrosive sublimate), when the mercury removes two molecules of cyanogen, and the chlorine two atoms of potassium, the nitrous acid of the nitrite of soda entering into the residue of the ferricyanide, and converting it into nitroprusside of potassium, which, by double decomposition with the acetate of soda, yields acetate of potash and nitroprusside of sodium. The cyanide of mercury crystallises out first, and the nitroprusside of sodium may be obtained in crystals from the evaporated solution.

The more recent researches of Städeler have still further simplified the constitution of the nitroprussides. By the action of cyanide of potassium upon ferrous sulphate, he obtained an orange precipitate composed of $KFe_2''Cy_5$, in which two atoms of diatomic iron have replaced four atoms of monatomic potassium in five molecules of the cyanide; $5KCy + 2Fe''SO_4 = 2K_2SO_4 + KFe_2''Cy_5$.

When this precipitate was treated with nitrite of potash, it furnished nitroprusside of potassium; $K'Fe_2''Cy_5' + KNO_2 = K_2'Fe''(NO)'Cy_5 + FeO$.

According to this, the hypothetical radical of the nitroprussides would contain $Cy_5(NO)'Fe''$, representing ferricyanogen Cy_6Fe'' in which $(NO)'$ has replaced Cy'. The monatomic character of the NO is shown in the nitrite of potash KNO_2 or $K'(NO)'O''$. It will be observed that Städeler's formula for the nitroprussides differs from Hadow's only by a single atom of oxygen in Hadow's molecule, thus—



Double molecule of nitroprusside of potassium (Städeler), $K_4Fe_2N_2O_2Cy_{10}$
Nitroprusside of potassium (Hadow), $K_4Fe_2N_2O_3Cy_{10}$,

so that whereas Hadow believed in the substitution of nitrous acid (N_2O_3) for a part of the cyanogen, Städeler finds that it is really NO, the radical of the nitrous acid ($(NO)'(NO)'O''$) which replaces the cyanogen.

On the latter view, the diatomic character of the assumed radical $Cy_5'(NO)'Fe''$ is at once explained, for it evidently requires two atoms of potassium to complete the saturation of the Cy_5.

The nitroprusside of sodium is used as a test for the alkaline sulphides, with a very slight trace of which it gives a magnificent purple colour. Thus, an inch or two of human hair, fused with carbonate of soda before the blowpipe, will yield sufficient sulphide of sodium to strike a purple tint with the nitroprusside.

321. THE FULMINATES.—The violently explosive compound known as *fulminate of mercury*, which is so largely employed for the manufacture of percussion caps, is connected with the series of cyanogen compounds.

Preparation of fulminate of mercury.—This substance is prepared by the action of alcohol upon a solution of mercury in excess of nitric acid; and as this action is of a violent character, some care is necessary in order to avoid an explosion. On a small scale, the fulminate may be obtained without any risk by strictly attending to the following prescription:—

Weigh out, in a watch-glass, 25 grains of mercury, transfer it to a half-pint beaker, add half an ounce (measured) of ordinary concentrated nitric acid (sp. gr. 1·42), and apply a gentle heat. As soon as the last particle of mercury is dissolved, place the beaker upon the table, away from any flame, and pour into it, pretty quickly, at arm's length, 5 measured drachms of alcohol (sp. gr. 0·87). Very brisk action will ensue, and the solution will become turbid from the separation of crystals of the fulminate, at the same time evolving very dense white clouds, which have an agreeable odour, due to the presence of nitrous ether, aldehyde, and other products of the action of nitric acid upon alcohol. The heavy character of these clouds is caused by the presence of mercury, though in what form has not been ascertained; much nitrous oxide and hydrocyanic acid are evolved at the same time. When the action has subsided, the beaker may be filled with water, the fulminate allowed to settle, and the acid liquid poured off. The fulminate is then collected on a filter, washed with water as long as the washings taste acid, and dried by exposure to air.

The chemical change involved in the preparation of the fulminate is complicated by the formation of the secondary products of the action of nitric acid upon alcohol, but if these be left out of consideration, a clear idea of the reaction may be obtained.

The fulminate of mercury is found, on analysis, to contain mercury, carbon, nitrogen, and oxygen in proportions corresponding to the formula $HgC_2N_2O_2$; if the mercury be supposed to exist in the state of oxide, into which it would have been converted by the nitric acid, this formula might be written $HgO.C_2N_2O$. The formula for alcohol is C_2H_6O, and the fulminate of mercury appears to be derivable from alcohol by the exchange of $H_6{}'$ for $N_2{}'''$, and the addition of HgO. It has been remarked (p. 140) that the action of nitrous acid (N_2O_3) upon organic substances frequently results in the removal of H_3 from the substance in the form of water; and it may be supposed that this acid, resulting from the de-oxidation of the nitric acid by one portion of the alcohol, has acted upon another portion so as to eliminate the whole of its hydrogen, and to leave, in exchange, 2 atoms of nitrogen; thus, $C_2H_6O + N_2O_3 = C_2N_2O + 3H_2O$. It is evident that the combining value of the two atoms of triatomic nitrogen is equal to that of six atoms of hydrogen.* The substance C_2N_2O, supposed to be combined with the oxide of mercury (though never obtained in the separate state), has been named *fulminic acid*. The chemical constitution of the fulminate will be more advantageously discussed when its properties have been considered.

Properties of fulminate of mercury.—This substance is deposited in the above process in fine needle-like crystals, which often have a grey colour from the accidental presence of a little metallic mercury. It may be purified by boiling it with water, in which it is sparingly soluble, and allowing the fulminate to crystallise from the filtered solution. Very moderate friction or percussion will cause it to detonate violently, so that it must be kept in a corked bottle lest it should be exploded between the neck and the stopper. It is usually preserved in a wet state, with about one-fifth its weight of water. Its explosion is attended with a bright flash, and with grey fumes of metallic mercury. The simplest equation to represent the decomposition would be $HgC_2N_2O_2 = Hg + 2CO + N_2$; and its violence must be attributed to the sudden evolution of a large volume of gas and vapour from a small volume of solid, for the fulminate of mercury, being exceedingly heavy (sp. gr. 4·4), occupies a very small space when compared with the gaseous products of its decomposition,

* This view is supported by the circumstance, that fulminate of silver is abundantly formed when nitrous acid is passed into an alcoholic solution of nitrate of silver.

especially when the latter are expanded by the heat. The evolution of heat during the explosion, apparently in contradiction to the rule that heat is absorbed in decomposition, must be ascribed to the circumstance that the heat evolved by the oxidation of the carbon exceeds that absorbed in the decomposition of the fulminate. A temperature of 360° F. explodes fulminate of mercury, and the same result is brought about by touching it with a glass rod dipped in concentrated sulphuric or nitric acid. The electric spark of course explodes it.

Cap composition.—The explosion of the fulminate of mercury is so violent and rapid that it is necessary to moderate it for percussion-caps. For this purpose it is mixed with nitrate or chlorate of potash, the oxidising property of these salts possibly causing them to be preferred to any merely inactive substances, since it would tend to increase the temperature of the flash by burning the carbonic oxide into carbonic acid, and would thus ensure the ignition of the cartridge. For military caps, in this country, chlorate of potash is always mixed with the fulminate, and powdered glass is sometimes added to increase the sensibility of the mixture to explosion by percussion. Sulphide of antimony is sometimes substituted for powdered glass, apparently for the purpose of lengthening the flash by taking advantage of the powerful oxidising action of chlorate of potash upon that compound (p. 163). Since the composition is very liable to explode under friction, it is made in small quantities at a time, and without contact with any hard substance. After a little of the composition has been introduced into the cap, it is made to adhere and water-proofed by a drop of solution of shell-lac in spirit of wine.

If a thin train of fulminate of mercury be laid upon a plate, and covered, except a little at one end, with gunpowder, it will be found on touching the fulminate with a hot wire, that its explosion scatters the gunpowder, but does not inflame it. On repeating the experiment with a mixture of 10 grains of the fulminate and 15 grains of chlorate of potash, made upon paper with a card, the explosion will be found to inflame the gunpowder.

By sprinkling a thin layer of the fulminate upon a glass plate, and firing it with a hot wire, the separated mercury may be made to coat the glass, so as to give it all the appearance of a looking-glass.

Although the effect produced by the explosion of fulminate of mercury is very violent in its immediate neighbourhood, it is very slightly felt at a distance, and the sudden expansion of the gas will burst fire-arms, because it does not allow time for overcoming the inertia of the ball, though, if the barrel escape destruction, the projectile effect of the fulminate is found inferior to that of powder.

The fulminate of mercury is generally contaminated with oxalate of mercury (HgC_2O_4), which is one of the secondary products formed during its preparation.

Fulminate of silver is prepared by a process very similar to that for fulminate of mercury, but since its explosive properties are far more violent, it is not advisable to prepare so large a quantity. 10 grains of pure silver are dissolved, at a gentle heat, in 70 minims of ordinary concentrated nitric acid (sp. gr. 1·42) and 50 minims of water. As soon as the silver is dissolved, the heat is removed, and 200 minims of alcohol (sp. gr. 0·87) are added. If the action does not commence after a short time, a very gentle heat may be applied until effervescence begins, when the fulminate of silver will be deposited in minute needles, and may be

further treated as in the case of fulminate of mercury.* When dry, the fulminate of silver must be handled with the greatest caution, since it is exploded far more easily than the mercury salt; it should be kept in small quantities wrapped up separately in paper, and placed in a card-board box. Nothing harder than paper should be employed in manipulating it. The violence of its explosion renders it useless for percussion caps, but it is employed in detonating crackers. Fulminate of silver is sparingly soluble in cold water, but dissolves in 36 parts of boiling water.

If a minute particle of fulminate of silver be placed upon a piece of quartz, and gently pressed with the angle of another piece, it will explode with a flash and smart report.

A *throw-down* detonating cracker may be made by screwing up a particle of the fulminate of silver in a piece of thin paper, with some fragments obtained by crushing a common quartz pebble.

The explosion of fulminate of silver may be compared with that of the mercury salt, by heating equal quantities upon thin copper or platinum foil, when the fulminate of mercury will explode with a slight puff, and will not injure the foil, but that of silver will give a loud crack and rend a hole in the metal.

If a particle of fulminate of silver be placed upon a glass plate and touched with a glass rod dipped in oil of vitriol, it will detonate and leave a deposit of silver upon the glass.

When fulminate of silver is dissolved in warm ammonia, the solution deposits, on cooling, crystals of a *double fulminate of silver and ammonia*, $Ag(NH_4)C_2N_2O_2$, which is even more violently explosive, and is dangerous while still moist.

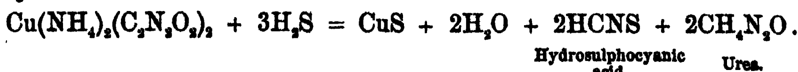
On adding chloride of potassium in excess to fulminate of silver, only half the silver is removed as chloride, and the *double fulminate of silver and potassium*, $AgKC_2N_2O_2$, may be crystallised from the solution. By the careful addition of nitric acid, the K may be replaced by H, and the *acid fulminate of silver*, $AgHC_2N_2O_2$, obtained, which is easily soluble in boiling water, and crystallises out on cooling; by boiling with oxide of silver, it is converted into the neutral fulminate.

Various other fulminates and double fulminates have been obtained. They are all more or less explosive.

Chemical constitution of the fulminates.—The fact of the existence of double fulminates and acid fulminates renders it necessary to write the formula of fulminate of silver, for example, $Ag_2C_2N_2O_2$, instead of AgCNO, in order to show that half of the silver is capable of being exchanged for another metal or for hydrogen. It will be seen that this formula would also represent two molecules of cyanate of silver (AgCNO), but the properties of this salt are entirely different from those of the fulminate. That a strong connection exists, however, between the fulminates and the cyanogen-compounds, is shown by several reactions. Thus, if fulminate of mercury be heated with hydrochloric acid, it is dissolved with evolution of a powerful odour of hydrocyanic acid, whilst mercuric chloride and oxalate, with hydrochlorate of ammonia, remain in the solution. Again, if an excess of fulminate of silver be acted on by hydrosulphuric acid, cyanic acid may be obtained in solution, and becomes converted into hydrosulphocyanic acid, when the hydrosulphuric acid is in excess. By decomposing the double fulminate of copper and ammonia $(Cu(NH_4)_2(C_2N_2O_2)_2)$ with hydrosulphuric acid, there are produced, hydro-

* If the nitric acid and alcohol are not of the exact strength here prescribed, it may be somewhat difficult to start the action unless two or three drops of red nitric acid (containing nitrous acid) are added. Standard silver (containing copper) may be used for preparing the fulminate.

sulphocyanic acid and urea, the latter having the same composition as cyanate of ammonia—



$$Cu(NH_4)_2(C_2N_2O_2)_2 + 3H_2S = CuS + 2H_2O + \underset{\text{Hydrosulphocyanic acid.}}{2HCNS} + \underset{\text{Urea.}}{2CH_4N_2O}.$$

These reactions have induced many chemists to regard the fulminates as compounds of the metallic oxides with an acid having the composition Cy_4O_2, intermediate in composition between the hypothetical anhydrous cyanic acid (Cy_2O) and the hypothetical anhydrous cyanuric acid (Cy_6O_3), but neither the anhydrous nor the hydrated fulminic acid has yet been obtained in a separate form. This view of the constitution of the fulminates, however, has the recommendation of simplicity, and enables the greater number of their reactions to be easily explained.

Fulminate of mercury dissolves when boiled with solution of chloride of potassium, and the solution, when evaporated, yields crystals of *fulminurate* or *isocyanurate* of potash, $KC_3N_3H_2O_3$, which has the same percentage composition as acid cyanurate of potash, $KH_2Cy_3O_3$, but the acid contained in fulminurate of potash forms only one series of salts, and is therefore monobasic. The fulminurates are feebly explosive. The production of fulminuric acid from the hypothetical fulminic acid may be represented by the equation—



$$2(H_2C_2N_2O_2) + H_2O = CO_2 + NH_3 + HC_3N_3H_2O_3.$$

PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF COAL.

322. Much of the extraordinary progress made by chemistry during the last half century must be attributed to the introduction and great extension of the manufacture of coal-gas. No other branch of manufacture has brought into notice so many compounds not previously obtained from any other source, and, above all, offering, at first sight, so very little promise of utility, as to press urgently upon the chemist the necessity for submitting them to investigation.

Although many important additions to chemical knowledge have resulted from the labours of those who have engaged in devising the best methods of obtaining the coal-gas itself in the state best fitted for consumption, far more benefit has accrued to the science from investigations into the nature of the secondary products of the manufacture, the removal of which was the object to be attained in the purification of the gas.

Of the compounds of carbon and hydrogen, very little was known previously to the introduction of coal-gas; and although the liquid hydrocarbons composing coal-naphtha were originally obtained from other sources, the investigation of their chemical properties has been greatly promoted by the facility with which they may be obtained in large quantities from that liquid. The most important of these hydrocarbons, *benzole* or *benzine*, was originally procured from benzoic acid; but it would have been impossible for it to have fulfilled its present useful purposes, but for the circumstance that it is obtained in abundance as a secondary product in the manufacture of coal-gas; for, leaving out of consideration the various uses to which benzole itself is devoted, it yields the *nitro-benzole*, so much used in perfumery, and from this we obtain *aniline*, from which many of the most beautiful dyes are now prepared.

The *naphthaline* found so abundantly in coal-tar possesses a peculiar interest, as having formed the subject of the beautiful researches by which

Laurent was led to propose the doctrine of substitution, which has since thrown so much light upon the constitution of organic substances.

We are also especially indebted to coal-tar for our acquaintance with the very interesting and rapidly extending class of volatile alkalies, of which the above-mentioned aniline is the chief representative, and for *phenic* or *carbolic acid*, from which are derived the large number of substances composing the phenyle-series.

The retorts in which the distillation of coal is effected are made either of cast-iron or of stoneware, generally having the form of a flattened cylinder, and arranged in sets of three or five, heated by the same coal fire (fig. 284). The charge for each retort is about two bushels, and is thrown on to the red-

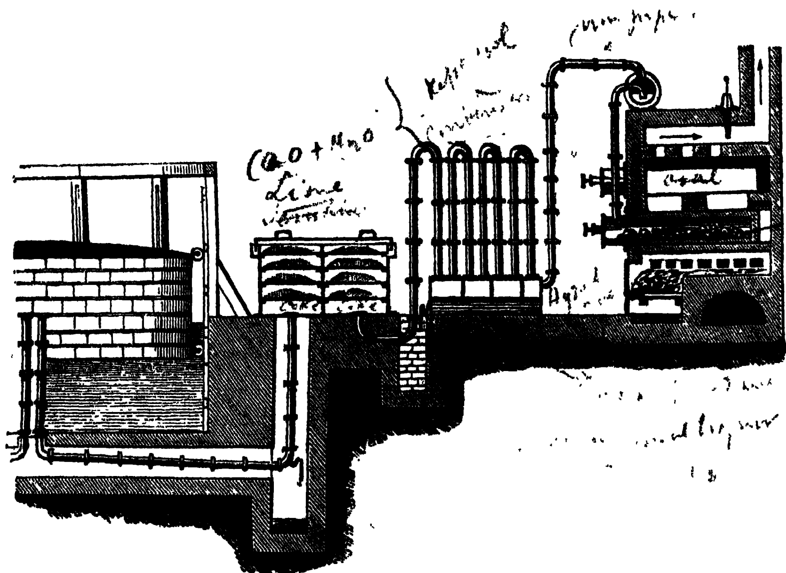


Fig. 284.—Manufacture of coal-gas.

hot floor of the retort, as soon as the coke from the previous distillation has been raked out; the mouth of the retort is then closed with an iron plate luted with clay. An iron pipe rises from the upper side of the front of the retort projecting from the furnace, and is curved round at the upper extremity, which passes into the side of a much wider tube, called the *hydraulic main*, running above the furnaces, at right angles to the retorts, and receiving the tubes from all of them. This tube is always kept half full of the tar and water which condense from the gas, and below the surface of this liquid the delivery tubes from the retorts are allowed to dip, so that although the gas can bubble freely through the liquid as it issues from the retort, none can return through the tube whilst the retort is open for the introduction of a fresh charge.

The aqueous portion of the liquid deposited in the hydraulic main is known as the *ammoniacal liquor*, from its consisting chiefly of a solution of various salts of ammonia, the chief of which is the sesquicarbonate; sulphide, cyanide, and sulphocyanide of ammonium are also found in it.

From the hydraulic main the gas passes into the *condenser*, which is

composed of a series of bent iron tubes kept cool either by the large surface which they expose to the air, or sometimes by a stream of cold water. In these are deposited, in addition to water, any of the volatile hydrocarbons and salts of ammonia which may have escaped condensation in the hydraulic main. Even in the condenser the removal of the ammoniacal salts is not complete, so that it is usually necessary to pass the gas through a *scrubber* or case containing fragments of coke, over which a stream of water is allowed to trickle in order to absorb the remaining ammoniacal vapours.

The *tar* which condenses in the hydraulic main is a very complex mixture, of which the following are some of the leading components—

	Boiling Point.	Formula.	Sp. Gr.
NEUTRAL HYDROCARBONS.			
Liquid.			
Benzole, ...	176° F.	C_6H_6	0·88
Toluole, ...	230°	C_7H_8	0·87
Xylole, ...	284°	C_8H_{10}	0·87
Isocumole,* . .	338°	C_9H_{12}	0·85
Solid.			
Naphthaline, . .	428°	$C_{10}H_8$	
Anthracene, . .	580°	$C_{14}H_{10}$	
Chrysene, ...	...	$C_{12}H_8$	
Pyrene, ...	...	$C_{15}H_{12}$	
ALKALINE PRODUCTS.			
Ammonia, ...	...	NH_3	
Aniline, ...	360°	C_6H_7N	1·02
Picoline, ...	271°	C_6H_7N	0·96
Quinoline, . . .	462°	C_9H_7N	1·08
Pyridine, ...	240°	C_5H_5N	
ACIDS.			
Carbolic acid, . .	370°	C_6H_6O	1·07
Kresylic ,, . .	397°	C_7H_8O	
Rosolic ,, . .	...	$C_{23}H_{22}O_4$	
Brunolic, ,, . .			
Acetic ,, . .	243°	$C_2H_4O_2$	1·06

The gas is now passed through the *lime-purifier*, which is an iron box with shelves, on which dry slaked lime is placed in order to absorb the carbonic acid and sulphuretted hydrogen, and the last portions of ammonia are removed by passing the gas through dilute sulphuric acid.

A great many other methods have been devised for the purification of the gas from sulphuretted hydrogen, but none appears to be so efficacious and economical as that which consists in passing the gas over a mixture of sulphate of iron (green vitriol or copperas), slaked lime, and saw-dust (which is employed to prevent the other materials from caking together).

* *Benzole*, originally derived from *benzoic acid*; *toluole*, from balsam of *tolu*; *xylole*, found among the products from *wood* (ξύλον); isocumole, isomeric with cumole, obtained from oil of *cummin*.

The lime decomposes the sulphate of iron, forming sulphate of lime and hydrated oxide of iron—



$$FeO.SO_3 + CaO.H_2O = FeO.H_2O + CaO.SO_3.$$

The action of air upon the mixture soon converts the oxide into sesquioxide of iron, which absorbs the sulphuretted hydrogen and the hydrocyanic acid, producing with the former sulphide of iron, and with the latter Prussian blue, or some similar compound. The sulphate of lime existing in this purifying mixture, is useful in absorbing any vapour of carbonate of ammonia from the gas, forming sulphate of ammonia and carbonate of lime.*

The action of the sulphuretted hydrogen on the sesquioxide of iron may be thus represented, $Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O$; and the circumstance which especially conduces to the economy of the process, is the facility with which the sulphide of iron may be reconverted into the sesquioxide by mere exposure to the action of atmospheric oxygen, for $2FeS + O_3 = Fe_2O_3 + S_2$, thus reviving the power of the mixture to absorb sulphuretted hydrogen. Accordingly, if a small quantity of air be admitted into the purifier together with the gas, it reconverts the sulphide of iron into sesquioxide, and the oxidation is attended with enough heat to convert into vapour any benzole which may have condensed in the purifying mixture, and of which the illuminating value would otherwise be lost. The same purifying mixture may thus be employed to purify a very large quantity of gas, until the separated sulphur has increased its bulk to an inconvenient extent, when it is distilled off in iron retorts. The various processes which have been devised for the removal of the bisulphide of carbon vapour are mentioned at p. 219.

The purified gas is passed into the gasometers, from which it is supplied for consumption.

In the manufacture of coal-gas, attention is requisite to the temperature at which the distillation is effected, for if it be too low, the solid and liquid hydrocarbons will be formed in too great abundance, not only diminishing the volume of the gas, but causing much inconvenience by obstructing the pipes. On the other hand, if the retort be too strongly heated, the vapours of volatile hydrocarbons, as well as the olefiant gas and marsh-gas, may undergo decomposition, depositing their carbon upon the sides of the retort, in the form of gas-carbon, and leaving their hydrogen to increase the volume and dilute the illuminating power of the gas.

These effects are well exemplified in the following analyses of the gas collected from Wigan cannel coal at different periods of the distillation:—

In 100 volumes.	1st hour.	5th hour.	10th hour.
Olefiant gas and volatile hydrocarbons,	13·0	7·0	0·0
Marsh-gas, ...	82·5	56·0	20·0
Carbonic oxide, ...	3·2	11·0	10·0
Hydrogen, ...	0·0	21·3	60·0
Nitrogen, ...	1·3	4·7	10·0

The increase of the carbonic oxide after the first hour must be attributed to the decomposition of the aqueous vapour by the carbon as the temperature rises, and the increase of the nitrogen may probably be

* Sesquioxide of iron itself, derived from various natural and artificial sources, is also employed for the purification of coal-gas.

ascribed to the decomposition of the ammonia into its elements at a high temperature.

323. One of the most useful of the secondary products of the coal-gas manufacture, is the ammonia, and this process has been already noticed as a principal source of the ammoniacal salts found in commerce.

Next in the order of usefulness stands the coal-tar, which deserves attentive consideration, not only on that account, but because the extraction of the various useful substances from this complex mixture affords an excellent example of *proximate organic analysis*, that is, of the separation of an organic mixture into its immediate components.

For the separation of the numerous volatile substances contained in coal-tar, advantage is taken of the difference in their boiling points, which will be observed on examining the table at p. 445.

A large quantity of the tar is distilled in an iron retort, when water passes over, holding salts of ammonia in solution, and accompanied by a brown oily offensive liquid which collects upon the surface of the water. This is a mixture of the hydrocarbons which are lighter than water, viz., benzole, toluole, xylole, and isocumole, all having, as represented in the table at p. 445, a specific gravity of about 0·85. 100 parts of the tar yield, at most, 10 parts of this *light oil.*

As the distillation proceeds, and the temperature rises, a yellow oil distils over, which is heavier than water, and sinks in the receiver. This oil, commonly called *dead oil*, is much more abundant than the light oil, amounting to about one-fourth of the weight of the tar, and contains those constituents of the tar which have a high specific gravity and boiling point, particularly naphthaline, aniline, quinoline, and carbolic acid. The proportion of naphthaline in this oil augments with the progress of the distillation, as would be expected from its high boiling point, so that the last portions of the oil which distil over become nearly solid on cooling. When this is the case, the distillation is generally stopped, and a black viscous residue is found in the retort, which constitutes *pitch*, and is employed for the preparation of Brunswick black and of asphalt for paving.

The light oil which first passed over is rectified by a second distillation, and is then sent into commerce under the name of *coal naphtha*, a quantity of the heavy oil being left in the retort, the lighter oils having lower boiling points.

This coal naphtha may be further purified by shaking it with sulphuric acid, which removes several of the impurities, whilst the pure naphtha collects on the surface when the mixture is allowed to stand. When this is again distilled it yields the *rectified coal naphtha.*

This light oil, especially when distilled from cannel coal at a low temperature, contains, in addition to the hydrocarbons above enumerated, some belonging to the marsh-gas series (C_nH_{2n+2}), and others more recently brought to light, belonging to a series the general formula of which is C_nH_{2n-2}; but these last appear to be acted on by the sulphuric acid, employed to remove the basic substances from the light oil, in such a manner that they are converted into polymeric hydrocarbons, having the general formula $C_{2n}H_{4n-4}$, of which the three following have been particularly examined:—

Formula.	Boiling point.
$C_{12}H_{20}$	410° F.
$C_{14}H_{24}$	464°
$C_{16}H_{28}$	536°

The hydrocarbons, C_6H_{10}, C_7H_{12}, and C_8H_{14}, from which these appear to have been

formed by the action of sulphuric acid, would evidently be the higher homologues of acetylene, C_2H_2.

The distillation of cannel coal, and of various minerals nearly allied to coal, at low temperatures, is now extensively carried on for the manufacture of paraffine and paraffine oil. (*See Paraffine.*)

The separation of the hydrocarbons composing this naphtha is effected by a process in constant use for similar purposes, and known as *fractional distillation.*

This consists in distilling the liquid in a retort (A, fig. 285) through the tubulure of which a thermometer (T) passes, to indicate the temperature at which it boils. The first portion which distils over will, of course,

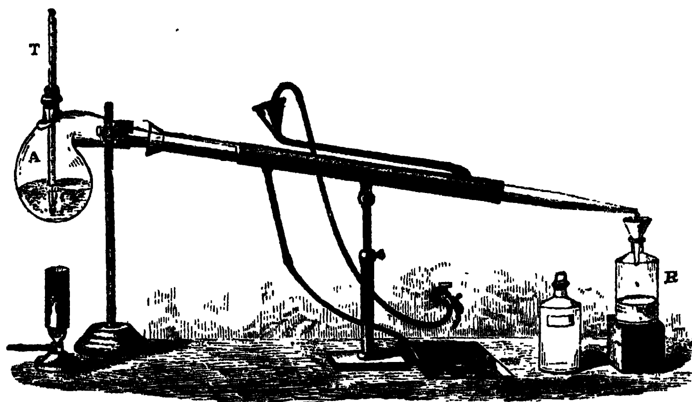


Fig. 285.—Fractional distillation.

consist chiefly of that liquid which has the lowest boiling point; and if the receiver (R) be changed at stated intervals corresponding to a certain rise in the temperature, a series of liquids will be obtained, containing substances the boiling points of which lie within the limits of temperature between which such liquids were collected.

When these liquids are again distilled separately in the same way, a great part of each is generally found to distil over within a few degrees on either side of some particular temperature, which represents the boiling point of the substance of which that liquid chiefly consists; and if the receivers be again changed at stated intervals, a second series of distillates will be obtained, the boiling points of which are comprised within a narrower range of temperature. It will be evident that, by repeated distillations of this description, the mixture will eventually be resolved into a number of liquids, each distilling over entirely at or about one particular degree, viz., the boiling point of its chief constituent.

To apply this to the separation of the constituents of light coal naphtha.

The crude light oil is first agitated with dilute sulphuric acid, which removes any basic substances present in it, and afterwards with a dilute solution of potash, to separate carbolic acid. The adhering potash is removed by shaking with water, and the naphtha is allowed to remain at rest, so that all the water may settle down, and the naphtha may be drawn off for distillation.

The naphtha begins to boil at about 160° F., but a small quantity distils over before the temperature has risen to 180°, when the receiver may be changed; between 180° and 200° a considerable quantity of the naphtha distils over, and at the latter degree the receiver is changed a second time. The receiver is changed at every 20°

throughout the distillation, until nearly the whole of the naphtha has passed over, which will be the case at about 360°.*

Ten unequal quantities of liquid will have been thus obtained, diminishing as the temperature rises.

Each of these must then be distilled in a smaller retort than the first, also provided with a thermometer.

The first portion (160° to 180°) will probably begin to boil at 150°, and will distil in great part before 160°, when the receiver may be changed. When the temperature reaches 170° it will probably be found that nothing remains worth distilling. The liquid passing over in this distillation between 160° and 170° may be added to that which is next to be distilled (180° to 200°).

The second portion (180° to 200°) will begin to boil at about 175°, and will distil over chiefly between that temperature and 185°, when the receiver may be changed. Nearly the whole will have passed over before 195°, and this last fraction may be added to that previously obtained from 200° to 220°.

When all the first series of liquids have been thus distilled, it will be found that the second series consists chiefly of six portions distilling between the following degrees of temperature, viz., 150°–160°, 175°–185°, 180°–190°, 240°–250°, 300°–310°, 340°–350°.

By another distillation of each of these portions, a third series of liquids will be formed, consisting chiefly of five portions distilling between the following points, viz., 145°–150°, 175°–180°, 230°–235°, 288°–293°, 336°–342°.

The portion distilling between 145° and 150° is comparatively small in quantity, and has not yet been fully examined.

That obtained between 175° and 180° is more abundant than either of the others, and is nearly pure benzole (C_6H_6).

The portion boiling between 230° and 235° is chiefly toluole (C_7H_8), whilst 288° to 293° gives xylole (C_8H_{10}), and 366° to 342° isocumole (C_9H_{12}).

In order to separate the benzole completely from the hydrocarbons which still adhere to it, the portion boiling between 175° and 180° is exposed to a temperature of 32°, when the benzole alone freezes, the other hydrocarbons remaining liquid, and being easily extracted by pressure.

A simpler method of separating liquids which have different boiling points consists in distilling them in a flask (F, fig. 286) connected with a spiral worm (W) of

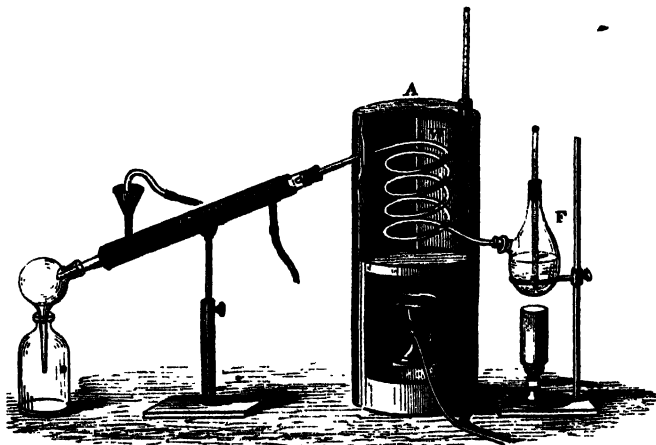


Fig. 286.—Fractional distillation.

pewter or copper, surrounded by water, or some other liquid, maintained at a temperature just above the boiling point of the particular liquid which is required to distil over. The greater part of the less volatile liquids will condense in the worm and run back into the flask. Thus, in extracting benzole from the light oil, the liquid in A might be kept at 180° F., when the toluole, &c., would be partly condensed in

* On the large scale, that portion of the naphtha which is distilled over between 180° and 250° F. is sold as benzole, and employed for the preparation of aniline.

the worm, and the portion which passed into the receiver would consist chiefly of benzole. When little more distilled over, the temperature of A might be raised to 230° and the receiver changed, when the distillate would contain toluole as its predominant constituent; and so on.

324. *Benzole.*—The pure benzole is a brilliant colourless liquid, exhaling a powerful odour of coal-gas; it boils at 176° F., and is very inflammable, burning with a smoky flame. It mixes readily with alcohol and wood-spirit, but not with water. Its property of dissolving caoutchouc and gutta percha renders it very useful in the arts, and it is an excellent solvent for the removal of grease, paint, &c., from clothes and furniture.

Benzole combines directly with chlorine to form a solid *chloride of benzole*, $C_6H_6Cl_6$, which is decomposed by an alcoholic solution of potash, yielding *chlorobenzole*, $C_6H_3Cl_3$.

By the action of an aqueous solution of hypochlorous acid upon benzole, a crystalline body has been obtained, having the composition $C_6H_9Cl_3O_3$, and called *trichlorhydrine of phenose.* When acted on by alkalies, this substance yields a sweet substance called *phenose*, isomeric with dry grape-sugar—



$$C_6H_9Cl_3O_3 + 3KHO = C_6H_{12}O_6 \text{ (Phenose)} + 3KCl.$$

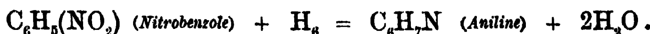
This substance has not been crystallised; it forms a deliquescent amorphous mass, which is easily soluble in water and alcohol, but insoluble in ether. It reduces the oxides of copper and silver like grape-sugar, and when acted on by nitric acid is converted into oxalic acid. Phenose has not been found capable of fermentation by yeast.

325. *Aniline.*—The chief purpose to which benzole is devoted is the preparation of aniline, which is subsequently converted into the brilliant dyes now so extensively used. It has been already noticed at p. 134, that when benzole is dissolved in fuming nitric acid, violent action takes place, and a dark red liquid is formed, from which water precipitates a heavy yellow oily liquid, smelling of bitter almonds, and known as *nitrobenzole*, which has the composition $C_6H_5(NO_2)$, and may be regarded as derived from benzole by the substitution of a molecule of nitric peroxide for an atom of hydrogen—



$$C_6H_6 \text{ (Benzole)} + HNO_3 = C_6H_5(NO_2) \text{ (Nitrobenzole)} + H_2O.$$

When nitrobenzole is placed in contact with diluted sulphuric acid and metallic zinc, the (nascent) hydrogen removes the whole of the oxygen, and two atoms of hydrogen are acquired instead, producing $C_6H_5NH_2$, or C_6H_7N, *aniline*—



$$C_6H_5(NO_2) \text{ (Nitrobenzole)} + H_6 = C_6H_7N \text{ (Aniline)} + 2H_2O.$$

That aniline has been produced may be shown by neutralising the excess of sulphuric acid with potash, and adding chloride of lime (hypochlorite of lime), which gives a fine purple colour with aniline.

The conversion of nitrobenzole into aniline on a large scale is more conveniently effected by gently heating it, in a retort, with water, iron filings, and acetic acid, when the deoxidising action of the acetate of iron $Fe(C_2H_3O_2)_2$, first produced, materially assists the change, this salt being converted into a basic peracetate of iron $2[Fe_2(C_2H_3O_2)_6]Fe_2O_3$, which is left in the retort, and the aniline may be distilled over, accompanied by water. At the close of the distillation a red oil passes over, which solidifies to a crystalline mass. This is *azobenzide*, C_6H_5N, originally obtained by distilling nitrobenzole with an alcoholic solution of potash.

(When nitrobenzole, in alcoholic solution, is reduced by zinc in the presence of hydrochloric acid, the solution neutralised by carbonate of soda and boiled with alcohol, a crystalline compound of aniline with chloride of zinc ($ZnCl_2.2C_6H_7N$) is obtained.)

Since aniline is only slightly soluble in water, and has the sp. gr. 1·02, the larger portion of it collects at the bottom of the liquid in the receiver, which is milky from the presence of minute drops of aniline in suspension. By pouring the contents of the receiver into a tall vessel, the greater part of the aqueous fluid may be separated, and the aniline may be purified by a second distillation, when the remaining water will pass over first, the boiling point of aniline being 360° F.

Aniline * presents many striking features; though colourless when perfectly pure, it soon becomes brown if exposed to the air; its odour is very peculiar and somewhat ammoniacal, and its taste is very acrid. A drop falling upon a deal table stains it intensely yellow. But the character by which aniline is most easily recognised, and that which leads to its useful applications, is the production of a violet colour with solution of chloride of lime, by which a very minute quantity of aniline may be detected. The exact nature of the chemical change connected with the production of this colour has not been determined, but it is known to be an oxidation, and a great number of processes have been patented from time to time for the production of crimson, purple, and violet dyes by the action of various oxidising agents upon aniline.

326. *Coal-tar dyes.*—The first dye ever manufactured from aniline on a large scale was that known as *mauve*, † or *aniline purple*, which is obtained by dissolving aniline in diluted sulphuric acid, and adding solution of bichromate of potash, when the liquid gradually becomes dark-coloured, and deposits a black precipitate, which is filtered off, washed, boiled with coal-naphtha to extract a brown substance, and afterwards treated with hot alcohol, which dissolves the mauve. The chemical change by which the aniline has been converted into this colouring-matter cannot at present be clearly traced, but the basis of the colour has been found to be a substance which has the composition $C_{27}H_{24}N_4$, and has been termed *mauvéine*. It forms black shining crystals, resembling specular iron ore, which dissolve in alcohol, forming a violet solution, and in acids, with production of the purple colour. Mauvéine combines with the acids to form salts; its alcoholic solution even absorbs carbonic acid gas. The *hydrochlorate of mauvéine*, $C_{27}H_{24}N_4,2HCl$, forms prismatic needles with a green metallic lustre.

Very brilliant red dyes are obtained from commercial aniline by the action of bichloride (tetrachloride) of carbon, bichloride of tin, perchloride of iron, chloride of copper, mercuric nitrate, corrosive sublimate, and hydrated arsenic acid. It will be noticed that all these agents are capable of undergoing reduction to a lower state of oxidation or chlorination, indicating that the chemical change concerned in the transformation of aniline into aniline red is one in which the aniline is acted on by oxygen or chlorine.

The easiest method of illustrating the production of aniline-red, on the small scale, consists in heating a few drops of aniline in a test-tube with a fragment of corrosive sublimate (perchloride of mercury), which soon fuses and acts upon the aniline to form an intensely red mass composed of aniline-red, calomel, and various secondary products. By heating this mixture with alcohol the red dye is dissolved, and a skein of silk or wool dipped into the liquid becomes dyed of a fine red, which is not removed by washing.

On the large scale, *Magenta* (as aniline-red is commonly termed) is generally prepared by heating aniline to about 320° F. with hydrated arsenic acid, when a dark semisolid mass is obtained, which becomes hard and brittle on cooling, and exhibits a green metallic reflection. This mass contains, in addition to aniline red, several secondary products of the action, and arsenious acid. On boiling it with water, a

* Aniline derives its name from *anil*, the Portuguese for indigo, from which it may be obtained by distillation with potash.

† French for marsh-mallow, in allusion to the colour of the flower.

splendid red solution is obtained, and a dark resinous or pitchy mass is left. If common salt be added to the red solution as long as it is dissolved, the bulk of the colouring matter is precipitated as a resinous mass, which may be purified from certain adhering matters by drying and boiling with coal naphtha. The red colouring matter is a combination of arsenic acid with a *colourless* organic base, which has been called *rosaniline*, and has the composition $C_{20}H_{19}N_3.H_2O$. If the red solution of arseniate of rosaniline be decomposed with hydrate of lime suspended in water, a pinkish precipitate is obtained, which consists of rosaniline mixed with arseniate of lime, and the solution entirely loses its red colour.

By treating the precipitate with a small quantity of acetic acid, the rosaniline is converted into *acetate of rosaniline* ($C_{20}H_{19}N_3,C_2H_4O_2$), forming a red solution, which may be filtered off from the undissolved arseniate of lime. On evaporating the solution to a small bulk, and allowing it to stand, the acetate is obtained in crystals which exhibit the peculiar green metallic lustre of the wing of the rose-beetle, characteristic of the salts of rosaniline. This salt is the commonest commercial form of Magenta ; its colouring power is extraordinary, a very minute particle imparting a red tint to a large volume of water. Silk and wool easily extract the whole of the colouring matter from the aqueous solution, becoming dyed a fast and brilliant crimson ; cotton and linen, however, have not so strong an attraction for it, so that if a pattern be worked in silk upon a piece of cambric, which is then immersed in a solution of Magenta and afterwards washed in hot water, the colour will be washed out of the cambric, but the red silk pattern will be left.

If a boiling solution of the acetate of rosaniline be mixed with excess of ammonia, the bulk of the rosaniline will be precipitated, but if the solution be filtered while hot, it deposits colourless needles of rosaniline, which become red when exposed to the air, from absorption of carbonic acid, and formation of the red carbonate of rosaniline.

Water dissolves but little rosaniline ; alcohol dissolves it abundantly, forming a deep red solution. Rosaniline forms two classes of salts with acids, those with one molecule of acid (*monacid* salts) being crimson, and those with three molecules (*triacid* salts) having a brown colour. Thus, if colourless rosaniline be dissolved in a little dilute hydrochloric acid, a red solution is obtained, which contains the monacid hydrochlorate of rosaniline, $C_{20}N_{19}H_3.HCl$; but if an excess of hydrochloric acid be added, the red colour disappears, and a brown solution is obtained, from which the triacid hydrochlorate, $C_{20}H_{19}N_3.3HCl$, may be crystallised in brown-red needles.

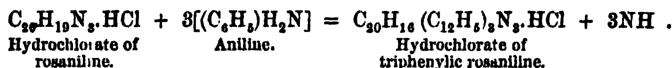
For experimental illustration of the properties of rosaniline, the liquid obtained by boiling a solution of the acetate with a slight excess of lime diffused in water, and filtering while hot, is very well adapted. This solution has a yellow colour, and may be preserved in a stoppered bottle without alteration. If air be breathed into it through a tube, the liquid becomes red from production of carbonate of rosaniline. Characters painted on paper with a brush dipped in the solution are invisible at first, but gradually acquire a beautiful rose colour.

When the red solution of hydrochlorate of rosaniline is slightly acidified with hydrochloric acid and placed in contact with zinc, the solution becomes colourless, the rosaniline acquiring two atoms of hydrogen, and becoming *leucaniline* (from λευκός, *white*) $C_{20}H_{21}N_3$, the hydrochlorate of which ($C_{20}H_{21}N_3.3HCl$) forms a colourless solution. Oxidising agents reconvert the leucaniline into rosaniline. It has been observed that *pure* aniline does not yield aniline-red when heated with corrosive sublimate or arsenic acid, it being necessary that it should contain another organic base, *toluidine* (C_7H_9N), which is derived from toluole (C_7H_8) in the same way in which aniline is derived from benzole. Since the benzole obtained from coal naphtha almost invariably contains toluole, the aniline obtained from it is very seldom free from toluidine. What share the toluidine has in the production of the red colour is not understood, but if the aniline be prepared with benzole derived from benzoic acid, and therefore free from toluole, no red is obtained. A mixture of 70 parts of toluidine with 30 of aniline, is said to answer best for the preparation of the red and violet-colouring matters. Such a mixture would contain two molecules of toluidine (C_7H_9N) and one of aniline (C_6H_7N), or $C_{20}H_{25}N_3$, only requiring the removal of H_6 by an oxidising agent to yield rosaniline $C_{20}H_{19}N_3$.

Aniline-yellow or *chrysaniline* (from χρύσεος, *golden*) is found among the secondary products obtained in the preparation of aniline-red. It forms a bright yellow powder resembling chrome-yellow, and having the composition $C_{20}H_{17}N_3$. It is nearly insoluble in water, but dissolves in alcohol. Chrysaniline has basic properties and dissolves in acids, forming salts. On dissolving it in diluted hydrochloric acid, and mixing the solution with the concentrated acid, a scarlet crystalline precipitate

of *hydrochlorate of chrysaniline* ($C_{20}H_{17}N_3.2HCl$) is obtained, which is insoluble in strong hydrochloric acid, but very soluble in water. A characteristic feature of chrysaniline is the sparing solubility of its nitrate. Even from a dilute solution of the hydrochlorate, nitric acid precipitates the nitrate of chrysaniline ($C_{20}H_{17}N_3.HNO_3$) in ruby-red needles.

Aniline-blue is produced when a salt of rosaniline (the commercial acetate, for example) is boiled with an excess of aniline, which converts the rosaniline ($C_{20}H_{19}N_3$) into *triphenylic rosaniline* ($C_{20}H_{16}(C_6H_5)_3N_3$), which may be regarded as having been formed by the introduction of three molecules of the hypothetical radical *phenyle* (C_6H_5) in place of three atoms of hydrogen, the latter having been evolved in the form of ammonia—



$$C_{20}H_{19}N_3.HCl + 3[(C_6H_5)H_2N] = C_{20}H_{16}(C_{12}H_5)_3N_3.HCl + 3NH .$$

Hydrochlorate of rosaniline. — Aniline. — Hydrochlorate of triphenylic rosaniline.

The hydrochlorate is an ordinary commercial form of aniline-blue; it has a brown colour, refuses to dissolve in water, but yields a fine blue solution in alcohol. If it be dissolved in an alcoholic solution of ammonia, the addition of water causes a white precipitate of the hydrated base, triphenylic rosaniline, $C_{20}H_{16}(C_6H_5)_3N_3.H_2O$, which becomes bluish when washed and dried.

Just as rosaniline yields leucaniline when acted on with nascent hydrogen, so triphenylic rosaniline yields triphenylic leucaniline ($C_{20}H_{18}(C_6H_5)_3N_3$); this is not basic like leucaniline, but a colourless neutral substance, which is reconverted into blue by oxidising agents. Compounds corresponding to triphenylic rosaniline, but containing methyle, ethyle, or amyle in place of phenyle, are obtained by digesting rosaniline with the iodides of these radicals, at a high temperature, in sealed tubes. Thus, by the action of iodide of ethyle (C_2H_5I) upon rosaniline, a blue crystalline body, insoluble in water, but soluble in alcohol, is obtained, which is a compound of ethyle iodide with triethylic rosaniline; $C_{20}H_{16}(C_2H_5)_3N_3$.



$$C_{20}H_{19}N_3 + 4C_2H_5I = C_{20}H_{16}(C_2H_5)_3N_3.C_2H_5I + 3HI .$$

Rosaniline. — Ethyl-iodate of tri-ethyl-rosaniline.

Aniline-violet appears to be formed in a similar manner. Other compounds have been obtained from aniline, presenting almost every variety of colour. A *green* dye is prepared by the action of a mixture of hydrochloric acid and chlorate of potash upon aniline, and under particular conditions a *black* may be obtained with the same agents. Another green has been made by acting upon Magenta with aldehyde.

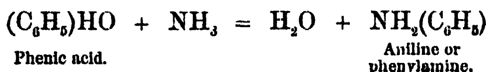
When a solution of acetate of rosaniline is treated with cyanide of potassium, it gradually loses its red colour, and deposits a white crystalline precipitate of a base which has been termed *hydrocyan-rosaniline*, having the formula $C_{21}H_{20}N_4$, and contains the elements of rosaniline and hydrocyanic acid; but this acid cannot be detected in it by the ordinary tests, leading to the belief that the new base should be regarded as leucaniline ($C_{20}H_{21}N_3$), in which one atom of hydrogen is replaced by a molecule of cyanogen ($C_{20}H_{20}(CN)N_3$). The hydrocyan-rosaniline is almost insoluble in water, and sparingly soluble in boiling alcohol. When precipitated from its salts by adding an alkali, it becomes pink on exposure to sunshine.

The present extensive application of aniline to the manufacture of these dyes affords a most striking example of the direct utility of pure chemistry to the arts; for only twelve or fifteen years ago, the name of this substance was not known to any but scientific chemists, whilst at present many tons are annually consumed to supply the wants of the dyers of silk and woollen goods.

327. Aniline ranks as a powerful organic base, combining readily with acids to form salts which are, generally speaking, easily crystallised. Like ammonia, it unites directly with the hydrated acids, without any separation of water; thus, the formula of sulphate of aniline is $2C_6H_7N.H_2O.SO_3$, just as that of sulphate of ammonia is $2NH_3.H_2O.SO_3$. With the hydrogen acids, also, aniline unites like ammonia, for hydrochlorate of aniline is $C_6H_7N.HCl$, and hydrochlorate of ammonia, $NH_3.HCl$; and exactly as the addition of potash to the salts of ammonia causes the sepa-

ration of ammoniacal gas, so when added to the salts of aniline, it precipitates that base in the form of oily drops, which render the liquid milky. This resemblance in disposition between aniline and ammonia leads to the impression that they must be moulded after a common type, and, accordingly, aniline is often represented as formed from ammonia (NH_3) by the substitution of the compound radical phenyle (C_6H_5) for an atom of hydrogen, and, upon this supposition, is termed *phenylamine*, $NH_2(C_6H_5) = C_6H_7N$.

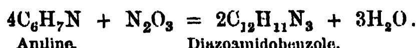
This view of the constitution of aniline is supported by the circumstance of its formation when phenic or carbolic acid is heated with ammonia in a tube hermetically sealed; for there is reason to believe that this acid, mentioned above as one of the chief acid products of the destructive distillation of coal, is phenylic hydrate $(C_6H_5)HO$, and its action upon ammonia would then be clearly explained by the equation—



$$(C_6H_5)HO + NH_3 = H_2O + NH_2(C_6H_5)$$

Phenic acid. Aniline or phenylamine.

When aniline is dissolved in alcohol and acted on by nitrous acid, two molecules of it loses three atoms of (monatomic) hydrogen, and acquire, in their stead, one atom of (triatomic) nitrogen, depositing a yellow compound, which has been called *diazoamidobenzole*—



$$4C_6H_7N + N_2O_3 = 2C_{12}H_{11}N_3 + 3H_2O.$$

Aniline. Diazoamidobenzole.

When the nitrous acid acts upon a hot solution, a base is formed isomeric with the above, and called *amido-diphenylimide*, which is identical with a yellow colouring matter obtained by the action of stannate of soda upon a salt of aniline. Its slightly acid solutions impart an intensely yellow colour to silk or wool, which is removed by heat, the base being volatile. The action of nitrous acid on aniline affords an example of a general method of producing compounds in which nitrogen is substituted for hydrogen.

Accompanying the aniline in coal tar, there are found three other bases, viz., *pyridine*, *picoline*, and *quinoline*. It will be seen that picoline (C_6H_7N) is isomeric with aniline, from which, however, it differs in a very striking manner, for its salts are by no means easily crystallisable, and it furnishes no violet colour with oxidising agents, such as chloride of lime. Picoline occurs among the products of the distillation of bones. Quinoline is also formed when some of the vegetable alkaloids are distilled with hydrate of potash.

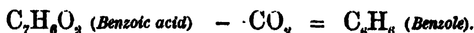
328. The other constituents of the light coal naphtha, viz., toluole, xylole, and isocumole, though not so important as benzole, on account of their practical applications, stand in a highly interesting relation to it and to each other.

These four liquids are members of a *homologous series*, that is, of a series *the members of which differ by the same number of atoms of the same elements*. Thus, toluole (C_7H_8) is seen to contain CH_2 more than benzole (C_6H_6), just as isocumole (C_9H_{12}) contains CH_2 more than xylole (C_8H_{10}). On reference to the table at p. 445, it will be seen that the boiling points of the members of this series are raised 54° F. for each addition of CH_2. Thus, xylole (C_8H_{10}) boils at 284°, or 54° higher than toluole (C_7H_8), which boils at 230°, whilst benzole (C_6H_6) boils at 54° below this, or 176°.

The members of this group are also intimately connected with those of another homologous series, known as *aromatic acids*, including—

Benzoic acid, . .	$C_7H_6O_2$
Toluic acid, . .	$C_8H_8O_2$
Cuminic acid, . .	$C_{10}H_{12}O_2$.

By distilling each of these acids with hydrate of baryta, the corresponding hydrocarbon is obtained, a molecule of carbonic acid being removed by the baryta; thus,



$$C_7H_6O_2 \text{ (Benzoic acid)} - CO_2 = C_6H_6 \text{ (Benzole)}.$$

The similarity between this decomposition and that by which marsh-gas (CH_4) is derived from acetic acid ($C_2H_4O_2$) will be at once apparent (see p. 95).

Each member of this series of hydrocarbons, when acted upon by nitric acid, yields a nitro-compound corresponding in composition to nitrobenzole, and this, under the influence of reducing agents (such as acetate of iron, or the hydrosulphate of an alkaline sulphide) yields a base homologous with aniline.

Thus we have the three following homologous series:—

Hydrocarbon.		Nitro-compound.		Base.	
Benzole,	C_6H_6	Nitrobenzole,	$C_6H_5NO_2$	Aniline,	C_6H_7N
Toluole,	C_7H_8	Nitrotoluole,	$C_7H_7NO_2$	Toluidine,	C_7H_9N
Xylole,	C_8H_{10}	Nitroxylole,	$C_8H_9NO_2$	Xylidine,	$C_8H_{11}N$.

329. *Carbolic* or *phenic acid*, or *phenole* ($C_6H_6O_2$), derives its interest chiefly from its constituting a great part of the ordinary commercial kreasote (from κρέας, *flesh*, and σώζω, *to preserve*). It is also present in cow's urine, and in that of some other animals. It is found chiefly in the heavy or dead oil of coal tar (p. 447), particularly in that portion which distils over between 300° and 400° F., when the oil is submitted to fractional distillation, and it appears to be the carbolic acid which confers upon this heavy oil its valuable antiseptic properties, leading to its employment for the preservation of wood from decay.

In order to extract the acid from that portion of the dead oil which distils between 300° and 400° F., it is shaken with a hot concentrated solution of hydrate of potash and some solid hydrate of potash. A white crystalline mass is deposited, which is separated from the liquid portion and treated with a little water, when a solution of carbolate of potash is obtained. This is separated from a quantity of oil which floats above it, and decomposed with hydrochloric acid, when the carbolic acid separates as an oily layer upon the surface. This is drawn off, digested with a little fused chloride of calcium to remove the water, and distilled. The distilled liquid, when exposed to a low temperature, solidifies to a mass of long colourless needles, which are liquefied even by the warmth of the hand (93° F.).

Carbolic acid has the peculiar taste and smell of kreasote. It dissolves sparingly in water, but readily in alcohol. When a piece of deal is wetted with solution of carbolic acid, and afterwards with hydrochloric acid, it becomes blue on drying.

The genuineness of a commercial sample of carbolic acid may be tested by shaking about a drachm of it with half a pint of warm water, which will dissolve the pure acid entirely, but will leave any "dead oil" undissolved. A solution of one part of caustic soda in ten parts of water should dissolve five parts of pure carbolic acid.

When carbolic acid is shaken with one-fourth of its weight of water, and exposed

to a temperature of 39° F., it deposits six-sided prismatic crystals of a hydrate, $2C_6H_6O.H_2O$, which is soluble in water, alcohol, and ether, and fuses at 61° F.
The acid properties of carbolic acid are of a very feeble and doubtful character. It is more properly regarded as *phenylic alcohol* or phenyle hydrate $(C_6H_5)HO$.

Carbolic a 'd is very largely used as an antiseptic agent. In medicine it is found very valuable, especially for the treatment of putrid sores; and, i a mixture with sulphite of lime, it forms the substance known as *MacDougall's disinfectant.*

330. *Carbazotic acid.*—When carbolic acid is boiled with fuming nitric acid, the solution, on cooling, deposits beautiful yellow crystals of *carbazotic* or *picric acid,* also called *trinitrophenic* or *nitrophenisic acid,* because it appears to be formed from phenic acid by the substitution of $3NO_2$ for H_3, just a nitrobenzole is formed from benzole by the substitution of NO_2 for H.

The composition of picric acid, upon this view, would be expressed by the formula $HC_6H_2(NO_2)_3O$, the atom of hydrogen being capable of displacement by a metal, forming a picrate or carbazotate; thus if the acid be added to a solution of potash, a yellow precipitate of carbazotate of potash, $KC_6H_2(NO_2)_3O$, is obtained, which has led to the employment of this acid as a test for potash.

Carbazotic acid is not easily soluble in water, but dissolves readily in alcohol. Its solutions have the property of staining the skin and other organic matters yellow, which is turned to advantage by the silk-dyer. The intensely bitter taste of the acid has also led to its employment for the adulteration of beer, to simulate the bitter of the hop.

Carbazotic acid is a very common product of the action of nitric acid upon organic substances; indigo, silk, and many resins furnish it in considerable quantity. It is economically obtained in a pure state by the action of nitric acid upon Botany Bay gum, but considerable quantities are manufactured for the dyer by treating the crude carbolic acid from coal tar with nitric acid. Carbazotic acid, as might be anticipated from its composition, explodes when sharply heated, its carbon and hydrogen being oxidised by the nitric peroxide.

When carbazotic acid is distilled with chloride of lime, it yields a heavy colourless oil having a very pungent odour of mustard, and boiling at 248° F.* This substance has been called *chloropicrine*, and has the remarkable formula $CCl_3(NO_2)$, which may be represented as formed upon the type of marsh-gas, CH_4, in which three atoms of the hydrogen are replaced by chlorine, and the fourth by nitric peroxide. Chloropicrine is frequently met with among the products of the action of chlorinating agents upon organic substances. It is almost insoluble in water, but dissolves easily in alcohol and ether.

When an alcoholic solution of chloropicrine is acted on by sodium, it yields the subcarbonate of ethyle, and when treated with cyanide of potassium, it exchanges two atoms of chlorine for cyanogen, forming an unstable dark red semi-fluid substance, having the composition $CClCy_2(NO_2)$, which may be regarded as derived from marsh-gas (CH_4) by the substitution of two molecules of cyanogen, one atom of chlorine, and one molecule of nitric peroxide, for the four atoms of hydrogen.

It will be instructive to compare the composition of the most important

* 233°·6 (Hofmann).

members of the *phenyle series*, as that group of organic compounds is termed, which are derived from the hypothetical radical phenyle (C_6H_5)—

Benzole or hydride of phenyle, .	$H(C_6H_5)$
Aniline or phenylamine, . .	$NH_2(C_6H_5)$
Phenic acid, ...	$H(C_6H_5)O$.
Trinitrophenic or picric acid, .	$H[C_6H_2(NO_2)_3]O$.

It is evident that whilst aniline may be regarded as ammonia in which the hypothetical phenyle is substituted for an atom of hydrogen, phenic acid can be represented as formed from a molecule of water by the substitution of phenyle for half the hydrogen, and benzole may be represented as a molecule of hydrogen, HH, in which one of the atoms is replaced by phenyle.

Some specimens of the kreasote found in commerce boil at a higher temperature than carbolic acid; this is due to the presence of *kresylic acid* ($C_7H_8O_2$), corresponding to carbolic acid, but regarded as containing the hypothetical radical kresyle (C_7H_7) in place of phenyle. The analogy in composition is attended with a resemblance in properties, for kresylic acid has the same antiseptic property as carbolic acid, and is applicable to similar purposes. When acted on by nitric acid, it yields *trinitrokresylic acid* ($HC_7H_4(NO_2)_3O$), just as carbolic acid gives trinitrophenic acid ($HC_6H_2(NO_2)_3O$).

331. *Naphthaline.*—The most prominent constituent of the heavy oil of coal tar is the naphthaline, which is easily procured in a pure state from the portions obtained at the close of the distillation, by simply pressing the semisolid mass to remove any liquid hydrocarbons, and boiling with alcohol, from which the naphthaline crystallises on cooling in brilliant pearly flakes, which may be still further purified by the process of sublimation.

In itself naphthaline is not very interesting, being a remarkably indifferent substance,* but it has been made the subject of several beautiful investigations which have thrown much light upon the action of chemical agents on organic compounds in general.

The most important of these researches is that upon the action of chlorine and bromine on naphthaline, which originated the now almost universally accepted doctrine of substitution, and fully established the fact, that an element may be replaced in a given compound by an equivalent quantity of another element of a totally different chemical character.

Thus, by the action of chlorine upon naphthaline, the hydrogen is removed in the form of hydrochloric acid, and there are obtained six new compounds by the progressive substitution of chlorine for the hydrogen, which Laurent distinguished by names indicating the number of atoms of chlorine present by means of the different vowels in the last syllable, introducing a new penultimate syllable when the vowels were exhausted, as will be seen in the following list:—

Naphthaline, . .	$C_{10}H_8$	Chlonaphtuse, . .	Wanting
Chlonaphtase, . .	$C_{10}H_7Cl$	Chlonaphthalase, . .	$C_{10}H_2Cl_6$
Chlonaphtese, . .	$C_{10}H_6Cl_2$	Chlonaphthalese, . .	Wanting
Chlonaphtise, . .	$C_{10}H_5Cl_3$	Chlonaphthalise, . .	$C_{10}Cl_8$.
Chlonaphtose, . .	$C_{10}H_4Cl_4$		

It will be observed that the original naphthaline type is here preserved

* A new crimson dye, *Magdala*, has been prepared from naphthaline.

throughout, the sum of the atoms being always 18, and the number of carbon atoms 10.

One of the most unexpected results of Laurent's investigation was the discovery that some of these compounds may be obtained in several distinct forms or modifications, which are isomeric, or have the same composition, but exhibit very different properties. Thus, there are seven varieties of chlonaphtese, all containing $C_{10}H_6Cl_2$, and yet differing from each other as much as substances not having the same composition. Two of them are liquids, and the five solid forms all fuse at different temperatures, ranging between 88° and 214° F. Seven different forms of chlonaphtise likewise exist, and four of chlonaphtose.

To account for this, Laurent supposed it to be by no means indifferent which particle of hydrogen has been removed from the compound, believing each to have its assigned place and specific function. Thus it may easily be conceived that the replacement of different particles of hydrogen by chlorine should give the seven modifications of chlonaphtese—

Naphthaline,	$C_{10}HHHHHHHH$
Chlonaphtese α,	$C_{10}ClClHHHHHH$
Chlonaphtese β,	$C_{10}HHClClHHHH$,

and so on. Other more recent investigations have given greater probability to this hypothesis.

Bromine, as might be anticipated, yields results similar to those with chlorine; but it could not have been predicted that substitution compounds might be obtained in which one part of the hydrogen is replaced by chlorine and the other by bromine. Thus, by acting upon a chlorine substitution compound with bromine, or *vice versâ*, the following substances were produced:*—

Chlorebronaphtise,	$C_{10}H_5Cl_2Br$
Chlorebronaphtose,	$C_{10}H_4Cl_2Br_2$
Chloribronaphtose,	$C_{10}H_4Cl_3Br$
Bromechlonaphtuse,	$C_{10}H_3Br_2Cl_3$
Bromachlonaphtose,	$C_{10}H_4BrCl_3$

It will be observed that chloribronaphtose and bromachlonaphtose have the same composition, though they possess different properties, and are obtained in very different ways, the former being procured by the action of bromine on chlonaphtise ($C_{10}H_5Cl_3$), and the latter by the action of chlorine upon bronaphtese ($C_{10}H_6Br_2$). Another confirmation is thus obtained of the belief, that upon the position of the hydrogen which is replaced, depends the character of the resulting compound.

Naphthaline is capable of direct union with chlorine to form two *chlorides of naphthaline*, having the formulæ $C_{10}H_8Cl_2$ and $C_{10}H_8Cl_4$, which may obviously be regarded as composed of substitution products combined with hydrochloric acid.

When acted upon by nitric acid, naphthaline furnishes three substitution products, in which one, two, and three atoms of hydrogen are replacd by NO_2; and each of these compounds, under the influence of reducing

* In naming these compounds, Laurent proceeded upon the same principle. The vowel immediately after the syllable *chlor-* or *brom-*, indicating the number of atoms of that element, whilst the vowel in the last syllable shows how many atoms of hydrogen have been replaced. The name begins with *chlor-* when the compound has been obtained by the action of bromine upon a chlorine substitution product, and *vice versâ*.

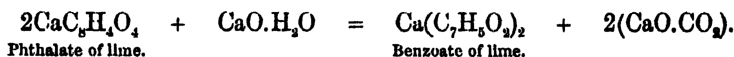
agents, yields a base, just as nitrobenzole, under similar treatment, yields aniline.

By prolonging the action of boiling nitric acid upon naphthaline, and evaporating the solution, crystals of *naphthalic* or *phthalic acid*, $H_2C_8H_4O_4$, are obtained. Through this acid, naphthaline is connected with the phenyle series; for when phthalic acid is heated with lime, it is resolved into carbonic acid and benzole—



$$\underset{\text{Phthalic acid.}}{H_2C_8H_4O_4} + 2CaO = \underset{\text{Benzole.}}{C_6H_6} + 2(CaO.CO_2).$$

Moreover, by digesting phthalate of lime with hydrate of lime at an elevated temperature for several hours, it is converted into benzoate and carbonate of lime—



$$\underset{\text{Phthalate of lime.}}{2CaC_8H_4O_4} + CaO.H_2O = \underset{\text{Benzoate of lime.}}{Ca(C_7H_5O_2)_2} + 2(CaO.CO_2).$$

Anthracene or *Paranaphthaline*, $C_{14}H_{10}$, which is found among the last products of the distillation of coal tar, differs from naphthaline in being almost insoluble in alcohol, and fusing only at 356° F., whilst naphthaline fuses at 174° F.*

Chrysene and *pyrene* are obtained at the close of the distillation of coal tar; they are crystalline solids not possessing any special importance, and have also been observed among the products of the destructive distillation of fatty and resinous bodies.

DESTRUCTIVE DISTILLATION OF WOOD.

332. The destructive distillation of wood may be advantageously studied in order to gain an insight into the effects of heat upon organic substances comparatively free from nitrogen, just as that of coal may serve as a general illustration of the behaviour of nitrogenised bodies under similar treatment.

The principal distinction between the two cases will be found to consist in the absence of basic substances from the products of the distillation of non-nitrogenised bodies.

All varieties of wood (freed from sap) consist essentially of *cellulose*, *lignine*, and mineral substances or ash. The cellulose ($C_6H_{10}O_5$) composes the wood-cells, and is therefore the most important constituent of the wood, the lignine being the material with which these cells are lined, and which appears to have a great influence upon the hardness of woods, being more abundant in the harder varieties, and particularly in such hard appendages as nut-shells. Lignine is far more easily dissolved by alkalies than cellulose, which is scarcely affected by them, but it has not hitherto been found possible to isolate the lignine in a state of purity for the purpose of determining its exact composition, since it is always accompanied in the wood by resinous matters, giving rise to the differences of colour in woods, and by a small quantity of nitrogenised matter, and of ash deposited with it from the sap.

The following results of the analysis of several woods will exhibit their general correspondence in composition:—

* The production of alizarine from anthracene will be noticed hereafter.

Wood dried in vacuo *at* 284° F.

	Beech.	Oak.	Birch.	Aspen.	Willow.
Carbon, ...	49·46	49·58	50·29	49·26	49·93
Hydrogen, . . .	5·96	5·78	6·23	6·18	6·07
Oxygen, ...	42·36	41·38	41·02	41·74	39·38
Nitrogen, . . . } Sulphur, . . . }	1·22	1·23	1·43	0·96	0·95
Ash, ...	1·00	2·03	1·03	1·86	3·67
	100·00	100·00	100·00	100·00	100·00

Cellulose in a nearly pure condition constitutes cotton, linen, and the best kinds of (unsized) paper, since the processes to which the woody fibre is subjected in the preparation of these materials, destroy and separate the less resistant lignine and the matters which accompany it.

On comparing the composition of wood with that of coal, it will be obvious that the large proportion of oxygen in the former must give rise to a great difference in the products of destructive distillation. Accordingly, it is found that water, carbonic oxide, carbonic acid, and acetic acid, all highly oxidised bodies, are produced in large quantity, and that the gaseous products of the distillation of wood burn with far less light than those from coal, in consequence of the smaller proportion of the heavier hydrocarbons.

The principal products of the action of heat upon wood are—

Wood Tar.

Solids.

Paraffine, . .	C_xH_{2x+2}	Pyrene, . . .	$C_{15}H_{12}$
Naphthaline, .	$C_{10}H_8$	Chrysene, . . .	$C_{12}H_8$
Cedriret,		Resin,	
Pittacal,			

Liquids.

Toluole, . .	C_7H_8	Pyroligneous or acetic acid, .	$C_2H_4O_2$
Xylole, . .	C_8H_{10}	Wood naphtha, .	CH_4O
Cymole, . .	$C_{10}H_{14}$	Acetate of methyle, .	$CH_3.C_2H_3O_2$
Kreasote, . .	C_7H_8O	Formiate of methyle,	$CH_3.CHO_2$
Picamar,		Acetone, . . .	C_3H_6O
Kapnomor, . .	$C_{10}H_{11}O$	Water,	
Eupione, . .	C_5H_{12}		

Gases.

Marsh-gas, ...	CH_4
Carbonic oxide, ...	CO
Carbonic acid, ...	CO_2

Of these products, by far the most important are the pyroligneous acid, the wood naphtha, and acetone.

The distillation of wood with a view to the preparation of these substances, is conducted in the manner described in the section on wood charcoal (p. 62), when the distillate separates into two portions, the heavier insoluble part constituting the wood tar, whilst the light aqueous layer contains the pyroligneous acid, naphtha, and acetone.

On distilling this, the two last, boiling respectively at 150° and 133°

F., first distil over, and then the acetic acid, which boils at 243° F. The acid so obtained, however, is contaminated with tarry matters, which communicate the peculiar odour of wood smoke, and adapt it especially for the preservation of meat. In order to obtain pure acetic acid, this crude acid is neutralised with carbonate of soda, and the acetate of soda thus obtained is moderately heated to expel the foreign substances. It is then further purified by solution in water and crystallisation, and is distilled with sulphuric acid, which converts the soda into sulphate, leaving the acetic acid to distil over.

333. *Wood naphtha—Methylic alcohol.*—In order to obtain the wood naphtha (or *pyroligneous ether*, or *wood spirit*, or *pyroxylic spirit*), the portion which distils over below 212° F. is rectified in a still containing chalk, which retains the acetic acid as acetate of lime.

The wood naphtha so obtained generally consists chiefly of *methylic alcohol* (CH_4O), but contains also acetone, acetate of methyle, and certain oily substances which impart to it a peculiar odour, and cause it to become milky when mixed with water. Wood generally yields about one part of naphtha to twenty of acetic acid. In order to obtain the pure methylic alcohol, chloride of calcium is dissolved to saturation in the crude wood spirit, when a definite crystallisable compound is formed, of 4 molecules of methylic alcohol and 1 of chloride of calcium, $CaCl_2.4CH_4O$. This is heated in a retort, placed in a vessel of boiling water, as long as any acetone and acetate of methyle pass over, the above compound not being decomposed at 212° F. An equal weight of water is then added to the residue in the retort, and the distillation continued, when the methylic alcohol distils over, accompanied by water, and the chloride of calcium remains in the retort. The diluted methylic alcohol is digested for some time with powdered quick-lime, and again distilled, when it is obtained in a state of purity.

The useful applications of crude wood naphtha depend upon its burning with a nearly smokeless flame in lamps (though as a source of heat only, not of light), and upon its power of dissolving most resinous substances employed in the preparation of varnishes, stiffening for hats, &c.

Methylic alcohol is the first member of the very important homologous series of alcohols, of which ordinary alcohol or spirit of wine is the type, and the consideration of which may be postponed until the chemical history of that alcohol shall have been studied. The designation of methylic alcohol supposes the existence in the pyroligneous spirit of a compound radical *methyle** (CH_3), of which methylic alcohol is the hydrate, $(CH_3)HO$. This view is by no means unsupported by experimental evidence; for if wood spirit be distilled with four parts of concentrated sulphuric acid, it yields a gas, the composition of which is represented by the formula, $(CH_3)_2O$, and this may be regarded as the oxide of methyle. Again, if wood spirit be distilled with iodine and phosphorus, the hydriodic acid formed (see p. 179) acts upon the hydrate of methyle, producing the compound CH_3I, *iodide of methyle.* When this is heated in contact with zinc, iodide of zinc is produced, and a gas, having the composition CH_3, which is that of the radical methyle, is obtained. (This important question of compound radicals will be more fully discussed hereafter.)

* From *μέθυ, wine; ὕλη, wood.* The termination *-yle* is generally bestowed upon compound radicals, because ὕλη is put metaphorically for *matter.* Thus, *ethyle* is meant to imply the matter from which ether compounds are derived.

A sulphide, bisulphide, chloride, bromide, and cyanide of methyle, may also be obtained, as well as compounds of the oxide of methyle with sulphuric, nitric, acetic, &c., acids. The methyle series is, in fact, perfectly parallel with the ethyle series, the members of which are far more important, and will therefore be more particularly considered hereafter.

One of the most interesting compounds derived from wood spirit is the *salicylate of methyle*, or *oil of winter green* ($CH_3.C_7H_5O_3$), which is extracted from the flowers of the *Gaultheria procumbens*, and was one of the first vegetable products to be prepared artificially by the chemist. It is obtained by distilling wood spirit with sulphuric acid and salicylic acid ($HC_7H_5O_3$), the latter acid being formed by the action of fused hydrate of potash upon the salicine ($C_{13}H_{18}O_7$) extracted from willow bark.

It will be noticed that the *formiate of methyle*, $CH_3.CHO_2$, would have the same *composition* as acetic acid, $HC_2H_3O_2$, though they are very different in *constitution*. An excellent illustration is here afforded of the distinction between an *empirical* and a *rational formula*, the former simply denoting the composition of a substance, without regard to the arrangement of its components, which is always indicated by the rational formula. Thus, the empirical formula of acetic acid, as well as of formiate of methyle, is $C_2H_4O_2$, but the rational formula of the latter is $CH_3.CHO_2$, showing it to be derived from formic acid (CH_2O_2), whilst the rational formula of acetic acid is $HC_2H_3O_2$. Such compounds are often said to be *metameric*, the term *isomeric* being usually applied to compounds having the same composition, but which are not known to possess a different constitution, such as oil of turpentine and many of the essential oils.

334. *Paraffine* (C_xH_{2x+2}) is a beautiful, semi-transparent, waxy substance, which distils over with the last portions of the tar from wood, and may be obtained in larger quantity by distilling peat, as well as from the mineral known as *Boghead cannel*. It is also found abundantly in the petroleum or mineral naphtha imported from Rangoon.

In order to extract the paraffine from wood tar, advantage is taken of its great resistance to the action of most chemical agents,* for which purpose the later portions of the distillate are moderately heated with concentrated sulphuric acid, which decomposes and chars most of the substances mixed with the paraffine, and allows the latter to collect as an oily layer upon the surface; this is allowed to cool and solidify, when it may be purified by pressure between blotting paper, and solution in a hot mixture of alcohol and ether, from which it is deposited, on cooling, in brilliant plates.

Paraffine fuses at 110° F., and may be distilled at a higher temperature; it burns, like wax, with a very luminous flame, and is employed as a substitute for wax in the manufacture of candles. It is insoluble in water, and dissolves sparingly in alcohol, ether being the best solvent for it.

It will be seen from the formula above given for paraffine, that the exact number of atoms of carbon and hydrogen contained in it is unknown, since it does not form definite compounds with other substances, and therefore its exact molecular weight cannot be ascertained; it is known, however, to belong to the marsh-gas series.

The substance known as *paraffine oil*, which is used for lubricating machinery, is the less volatile portion of the hydrocarbons obtained by

* To which it owes its name, from *parum, little; affinis, allied,*

the destructive distillation of Boghead cannel (found at Bathgate, near Edinburgh). The more volatile portion of the hydrocarbons so obtained is employed for illuminating purposes.

Acetone will be described hereafter.

Of the other products of the destructive distillation of wood enumerated at p. 460, some have been described amongst the products obtained from coal, and the remainder have been but little studied, and have not received any useful application.

Eupione (C_5H_{12}) is a liquid lighter than water, and boiling at 116° F.

Kapnomor is an oily liquid, which boils at 360°.

Picamar is another oily liquid, heavier than water.

Cedriret is a red crystalline substance.

Pittacal is a blue solid.

Stockholm tar is collected during the carbonisation of pine wood, containing a large quantity of resin, the tar running off through an aperture at the lower part of the pit, in which the imperfect combustion of the wood is carried on. It differs from ordinary tar in containing large quantities of resin and turpentine, the latter being separated from it by distillation, and the residue constituting the *pitch* of commerce.

Petroleum.—There are found, in different parts of the earth, generally in or near the coal-formations, several solid or liquid hydrocarbons, probably formed during the conversion of vegetable remains into coal, some of which have received useful applications.

The Rangoon tar has already been noticed as containing a considerable quantity of paraffine; the liquid part of this tar, after distillation and treatment with oil of vitriol to remove hydrocarbons of the benzole series,* is the liquid in which potassium and sodium are preserved; it is commonly called *petroleum* or *rock-oil*, and appears to be a mixture of several hydrocarbons. Petroleum is also employed occasionally as a solvent for caoutchouc and resinous substances. In the neighbourhood of the Caspian sea there are several springs from which rock-oil flows, together with water, from the surface of which it is skimmed and sent into commerce.

American petroleum.—Within the last few years abundant supplies of petroleum have been obtained from wells and springs in Pennsylvania and Canada, and the demand for it to serve as an illuminating agent, and for the lubrication of machinery, has created a new branch of commerce, giving rise to the rapid growth of "oil cities" in the neighbourhood of the wells. These rock-oils have a very peculiar unpleasant odour, and appear to consist chiefly of hydrocarbons belonging to the homologous series of which marsh-gas (CH_4) is a member. Thus, the Pennsylvanian petroleum has furnished the hydrocarbons, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, C_8H_{18}, C_9H_{20}. In addition to these, the hydrocarbons, $C_{10}H_{20}$, $C_{11}H_{22}$, $C_{12}H_{24}$, homologous with olefiant gas (C_2H_4), have been obtained from it. Some of the members of the benzole series appear also to be present in the Canadian petroleum.

The mineral substance known as *bitumen* or *asphaltum* contains a hydrocarbon, apparently isomeric with oil of turpentine, together with a resinous substance, and a black matter resembling pitch, and containing oxygen. It is employed for making water-proof cements and black varnishes, being dissolved for this purpose in turpentine.

Bituminous shale, when distilled, furnishes products which, as far as they are known, are closely allied to those obtained from wood and coal.

* These hydrocarbons, when treated with oil of vitriol, form acids which are soluble in water. Thus benzole is converted into *sulphobenzolic acid*, $HC_6H_5.SO_3$.

OIL OF TURPENTINE AND SUBSTANCES ALLIED TO IT.

335. Turpentine is the generic name given to the viscous exudation obtained by incising the bark of various species of pine. Several varieties of turpentine are met with in commerce, of which the two best known are the common turpentine which is obtained from the Scotch fir, and Venice turpentine from the larch.

These are both solutions of *colophony* or common rosin ($C_{20}H_{30}O_2$) in the essential oil of turpentine ($C_{10}H_{16}$), and when distilled, yield from 75 to 90 per cent. of rosin, which remains in the retort, and from 25 to 10 per cent. of the essential oil, commonly sold as *spirits of turpentine.*

This essence of turpentine boils at 320° F., and floats upon water (sp. gr. 0·864), in which it is very sparingly soluble, its proper solvents being alcohol and ether. Its great inflammability renders it useful as a fuel for lamps, but the large proportion of carbon which it contains causes it to burn with a smoky flame, rendering it necessary either to employ lamps constructed especially to afford an extra supply of air to the flame, or to mix it with a certain proportion of alcohol. *Camphine* is distilled from the turpentine of the Boston pine.

The property of turpentine to dissolve resinous and fatty substances renders it exceedingly useful in the preparation of paints and varnishes, and for the removal of such substances from fabrics. It is also an excellent solvent for caoutchouc.

One of the most remarkable features of this essential oil is the facility with which it changes into isomeric or metameric modifications, exhibiting great differences in their physical and chemical properties.

When heated in a closed vessel to about 480° F. for some hours, oil of turpentine is converted into two isomeric modifications differing greatly from the original oil in the temperature at which they boil; for whilst oil of turpentine distils over entirely at 320° F., one of these modifications, known as *isoterebenthene*, boils at 350° F., and the other, *metaterebenthene*, at 660°.

When digested, in the cold, with a small proportion of oil of vitriol, oil of turpentine yields *terebene* and *colophene*, the former boiling at 320° F., but differing from oil of turpentine in its odour, which resembles thyme, and in its want of action upon polarised light.

Colophene has a far higher boiling point (600°), and is much heavier than turpentine (sp. gr. 0·940), from which it is also distinguished by its indigo-blue colour when seen obliquely, though it is colourless by directly transmitted light. Moreover, the specific gravity of the vapour of colophene is 9·52, whilst that of turpentine is 4·76, or one-half that of colophene, rendering it probable that if the composition of turpentine be $C_{10}H_{16}$ (= 2 vols.), that of colophene is $C_{20}H_{32}$ (= 2 vols.), a relation expressed by saying that colophene is *polymeric* with turpentine. Colophene is also obtained by the distillation of colophony,

The ordinary oil of turpentine appears to be really itself a compound of two isomeric hydrocarbons, for when hydrochloric acid gas is passed into it, two distinct isomeric compounds are formed, both expressed by the formula, $C_{10}H_{16}.HCl$, but one being a solid, and the other a liquid even at 0° F.

The solid compound, which is known as *artificial camphor* or *hydrochlorate of dadyle*, forms white prismatic crystals very similar to camphor, and when its vapour is passed over heated quick-lime, the latter removes the hydrochloric acid, and the hydrocarbon known as *camphilene* or *dadyle* (δᾴς, a pine-torch) is obtained, which is isomeric with oil of turpentine, but boils at 273° instead of 320° F., and is without any action upon polarised light.

The liquid compound formed by the action of hydrochloric acid upon oil of turpentine is called *hydrochlorate of peucyle;* and when distilled with quick-lime yields *terebilene* or *peucyle* (πεύκη, *the pine*), also isomeric with oil of turpentine, but without action on polarised light.

Although oil of turpentine is not miscible with water, it is capable of forming three compounds with it in different proportions. When the oil is long kept in contact with water, crystals are deposited which have the composition $C_{10}H_{16}.3H_2O$;

boiling water dissolves these, and deposits them in a prismatic form on cooling. The crystals fuse at about 217° F.; and when further heated, lose a molecule of water, yielding another crystalline hydrate, which sublimes without alteration at about 480° F. When exposed to the air this hydrate again absorbs a molecule of water.

By distilling the aqueous solution of either of the preceding hydrates with a little sulphuric acid, a liquid hydrate smelling of hyacinths is obtained; it contains $(C_{10}H_{16})_2H_2O$, and is called *terpinole.*

When oil of turpentine is exposed to the air, it slowly becomes solid, absorbing oxygen, and becoming converted into resinous bodies.

Common rosin or *colophony.**—This substance is composed of two isomeric acids known as *sylvic* and *pinic.* When common rosin is treated with cold alcohol, the greater portion of it is dissolved; and if the alcohol be evaporated, it leaves an amorphous substance, which is *pinic acid.* The residue, left undissolved by cold alcohol, is dissolved by hot alcohol, and deposited in colourless prisms, which are *sylvic acid.* These acids have the composition $HC_{20}H_{29}O_2$. The pinate and sylvate of soda obtained by dissolving rosin in solution of soda or carbonate of soda, are largely used in the manufacture of yellow soap, and of the size for paper-makers. By distilling common rosin with the aid of superheated steam, it is obtained nearly free from colour.

336. *The turpentine series of hydrocarbons.*—Oil of turpentine is the representative of a large class of hydrocarbons, derived like itself from the vegetable kingdom, and all having a percentage composition corresponding to the formula $C_{10}H_{16}$. All the individuals of this group resemble turpentine in their liability to suffer conversion into isomeric modifications, in their solidification by absorption of oxygen when exposed to the air, in their combination with water to form crystalline hydrates, and above all, in their tendency to form artificial camphors by combining with hydrochloric acid.

The *oils of bergamotte, birch, camomile, carraway, cloves, hops, juniper, lemons, orange, parsley, pepper, savin, tolu, thyme,* and *valerian,* contain the same hydrocarbon $C_{10}H_{16}$, generally accompanied, in the natural oil, by the product of its oxidation, bearing a relation to the hydrocarbon similar to that which colophony bears to turpentine.

These essential oils are generally extracted from the flowers, fruit, leaves, or seeds, by distillation with water, the portion of the plant selected being suspended in the still by means of a bag or perforated vessel, so that there may be no danger of its being scorched by contact with the hot sides of the still, and so contaminating the distillate with *empyreumatic* matters (ἐμπυρεύω, to scorch). The water which distils over always holds a little of the essential oil in solution, and it is in this way that the fragrant distilled waters of the druggist are obtained. When the essential oil is present in large proportion, it collects as a separate layer upon the surface of the water, from which it is easily decanted. The oil which is dissolved in the water may be separated from it by saturating the liquid with common salt, when the oil rises to the surface, or by shaking it with ether, which dissolves the oil and separates from the water, the ethereal solution floating upon its surface, and leaving the oil when the ether is evaporated.

In cases like that of jasmine, where the delicate perfume of the flower would be injured by the heat, the flowers are pressed between woollen

* Colophon, a city of Ionia.

cloths saturated with oil of poppy seeds, which thus acquires a powerful odour of the flower.

Bisulphide of carbon is also sometimes employed as a solvent for extracting the essential oils.

Oil of peppermint contains a hydrocarbon called *menthene* ($C_{10}H_{18}$); *essence of cedar-wood* contains *cedrene* ($C_{16}H_{26}$).

337. *Camphors.*—Closely allied to the essential oils are the different varieties of camphor, which appear to be formed by the oxidation of hydrocarbons corresponding to the essential oils.

Common camphor ($C_{10}H_{16}O$) is found deposited in minute crystals in the wood of the *Laurus camphora* or camphor laurel, from which it is obtained by chopping up the branches and distilling them with water in a still, the head of which is filled with straw, upon which the camphor condenses. It is purified by subliming it in large glass vessels containing a little lime.

Camphor passes into vapour easily at the ordinary temperature of the air, and is deposited in brilliant octahedral crystals upon the sides of the bottles in which it is preserved. It fuses at 347° F., and boils at 399° F., and is very inflammable, burning with a bright smoky flame. It is sometimes dissolved in the oil used for the lamps of magic lanterns, to increase its illuminating power. Camphor is lighter than water (sp. gr. 0·996), and whirls about upon its surface in a remarkable way, dissolving meanwhile very sparingly (1 part in 1000), alcohol and ether being its appropriate solvents.

When distilled with anhydrous phosphoric acid, camphor loses a molecule of water, and yields the hydrocarbon cymole ($C_{10}H_{14}$) homologous with benzole.

Borneo camphor ($C_{10}H_{18}O$) is obtained from the exudation of the *Dryobalanops camphora.* When this exudation is distilled, a hydrocarbon called *bornéne* ($C_{10}H_{16}$), isomeric with oil of turpentine, first passes over, and afterwards the camphor, which is neither so fusible nor so volatile as ordinary camphor, and emits quite a different odour; it also crystallises in prisms instead of octahedra, and may be converted into ordinary camphor by the action of nitric acid, which oxidises two atoms of hydrogen—



$$C_{10}H_{18}O \text{ (Borneo camphor)} - H_2 = C_{10}H_{16}O \text{ (Common camphor)}.$$

The Borneo camphor appears to have been formed by the combination of bornеène with water, for if this hydrocarbon be distilled with solution of potash, it combines with a molecule of water, and is converted into the camphor. On the other hand, when Borneo camphor is distilled with anhydrous phosphoric acid, it loses a molecule of water, and yields bornеène. It is interesting to remark that this hydrocarbon is also found in the essential oil of valerian.

The *oil of camphor* which accompanies the camphor distilled from the camphor laurel, contains an atom of oxygen less than common camphor, its formula being $(C_{10}H_{16})_2O$.

338. *Balsams.*—The vegetable exudations known as balsams are mixtures of essential oils with resins and acids probably produced by the oxidation of the oils.

Balsam of Peru contains an oily substance termed *cinnamèine* ($C_{27}H_{26}O_4$), a crystalline body, *styracine* (C_9H_8O), a crystalline volatile acid, the *cinnamic* ($C_9H_8O_2$), and a peculiar resin.

Balsam of Tolu also contains cinnamic acid and styracine, together with certain resins, which appear to have been formed by the oxidation of styracine.

Storax, also a balsamic exudation, contains the same substances, accompanied by a peculiar hydrocarbon, which has been named *styrole*, and has the composition C_8H_8. This liquid is characterised by a remarkable

change which it undergoes when heated to about 400° F., being converted into a colourless solid, *metastyrole*, which is polymeric with styrole, into which it is reconverted by distillation.

339. *Resins.*—Colophony is the best known member of the class of resins, which are generally distinguished by their *resinous* appearance, fusibility, inflammability, burning with a smoky flame, insolubility in water, and solubility in alcohol.

As to their chemical composition, they are all rich in carbon and hydrogen, containing generally a small proportion of oxygen, and appear to have been formed, like colophony (p. 465), by the oxidation of a hydrocarbon analogous to turpentine.

Most of the resins also resemble colophony in their acid characters, their alcoholic solutions reddening blue litmus paper, and the resins themselves being soluble in the alkalies. This is the case with *sandarach* and *guaiacum resin*, the former of which contains three, and the latter two, resinous acids.

Copal appears to contain several resins, some neutral and some acid, and is distinguished by its difficult solubility in alcohol, in which it can be dissolved only after long exposure to the vapour of the solvent; but if it be exposed to the air for some time, at a moderately high temperature, it absorbs oxygen, and becomes far more easily soluble. Copal is readily dissolved by acetone. *Animi* and *elemi* resins are somewhat similar in properties to copal.

All these resins are used in the manufacture of varnishes.

Guaiacum resin is distinguished by its tendency to become blue under the influence of the more refrangible and chemically active (violet) rays of the solar spectrum, as well as under that of certain oxidising agents, such as chlorine and ozone.

Lac, so much used in the arts, belongs to the class of resins, being the exudation of certain tropical trees punctured by an insect. In its crude natural state, encrusting the small branches, it is known as *stick-lac*, and has a deep red colour; when broken off the branches and boiled with water containing carbonate of soda, it furnishes a red colouring matter, very largely used in dyeing, leaving a resinous residue termed *seed-lac*, by fusing which the *shell-lac* is obtained. This resin is very complex, containing several distinct resinous bodies. It is largely used in the manufacture of hats, of sealing-wax, and of varnishes. The *lacquer* applied to brass derives its name from this resin, being an alcoholic solution of shell-lac, sandarach, and Venice turpentine. *Indian ink* is made by mixing lamp-black with a solution of 100 grains of lac in 20 grains of borax and 4 ounces of water.

Amber, a fossil resinous substance, more nearly resembles this class of bodies than any other, and contains several resinous bodies. It is distinguished by its insolubility, for alcohol dissolves only about one-eighth, and ether about one-tenth of it. After fusion, however, it becomes soluble in alcohol, and is used in this state for the preparation of varnishes.

The distinguishing peculiarity of amber is, that it yields *succinic acid*, $H_2C_4H_4O_4$ (*succinum, amber*), when digested with alkalies, distilled, or oxidised by nitric acid; in the latter case ordinary camphor is formed at the same time.

Succinic acid is also found in some of the resins of coniferous trees, and in the leaves of the wormwood. It is among the products of the action

of nitric acid upon most fatty and waxy substances, and is present in wines and other fermented liquors, being produced during the fermentation of sugar. The acid is characterised by the cough-provoking vapour which it emits when heated.*

Varnishes are prepared by dissolving resins in alcohol, or wood spirit, or acetone,† a little turpentine or some fixed oil being added to prevent the resin from cracking when the solvent has evaporated. In order to promote the solution of the resin, it is usually powdered before being treated with the solvent, and mixed with coarsely powdered glass to prevent it from becoming lumpy. *Methylated spirit* is now very generally used for the preparation of varnishes; it is simply spirit of wine, to which a little wood naphtha has been added, to deter persons from drinking it, and to prevent other frauds upon the Excise.

Benzoin, or gum benzoin, as it is erroneously called, is also a vegetable resinous product, and is distinguished by the presence of *benzoic acid* ($HC_7H_5O_2$), which may be obtained from it by heating the resin in an iron or earthen vessel (fig. 287) covered with a perforated sheet of stout paper, over which a drum or cone of paper is tied. When the heat of a sand-bath is applied, benzoic acid rises in vapour, and is condensed in beautiful feathery crystals in the paper drum. It may also be extracted by boiling the resin with water and lime, when the benzoic acid is dissolved in the form of benzoate of lime $Ca(C_7H_5O_2)_2$, and being but sparingly soluble in water, may be precipitated by adding hydrochloric acid to the filtered solution.

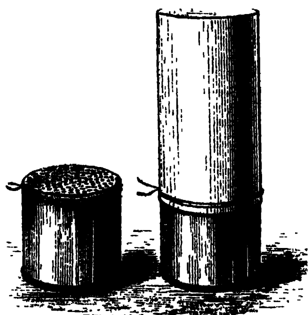


Fig. 287.

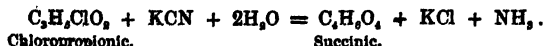
Benzoic acid is generally recognised by its feathery appearance and peculiar agreeable odour, though this does not really belong to the acid, but to a little essential oil which is not easily separated; the vapour of the acid itself is very irritating and produces coughing. It fuses when moderately heated, and burns with a smoky flame. Benzoic acid dissolves in about 200 parts of cold and 25 parts of boiling water. Alcohol and ether dissolve it easily.

The salts of benzoic acid, or *benzoates*, have no practical importance, but the behaviour of benzoic acid when distilled with an excess of lime or baryta has already been referred to as furnishing that important hydrocarbon, benzole (see p. 455).

Oil of Bitter Almonds, and its Derivatives.—Benzoyle Series.

340. Benzoic acid results from the oxidation of the essential oil of bitter almonds (C_7H_6O), which slowly absorbs an atom of oxygen from the air, and is converted into benzoic acid ($C_7H_6O_2$).

* Succinic acid has been obtained artificially by the action of cyanide of potassium upon a solution of chloropropionic acid;



$$\underset{\text{Chloropropionic.}}{C_3H_5ClO_2} + KCN + 2H_2O = \underset{\text{Succinic.}}{C_4H_6O_4} + KCl + NH_3.$$

† Acetone readily dissolves copal, mastic, and sandarach.

The formation of the essential oil of bitter almonds is one of the most interesting processes of vegetable chemistry.

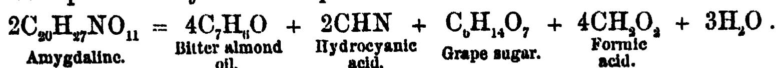
Both the bitter and the sweet almond contain a large quantity of a fixed oil, which may be extracted from them by pressure, but which has no particular taste or odour, and differs entirely from the essential oil of bitter almonds, being, in fact, very similar to ordinary olive oil. The residue, or almond-cake, which is left after expressing the oil, contains, in the case of the bitter almond only, a bitter principle, amounting to about $\frac{1}{10}$th of the weight of the almond, which may be extracted from the cake by hot alcohol, and may be crystallised from the solution; this substance is called *amygdaline*, and is represented by the formula $C_{20}H_{27}NO_{11}$, the crystals containing, in addition, three molecules of water.

Now, if the residue left after extracting the amygdaline with alcohol be mixed with water and distilled, it does not yield any essential oil, although this may be obtained in abundance from the original cake after maceration in water, particularly if it be digested with water for several hours before distillation.

The sweet almond, which contains no amygdaline, does not afford any essential oil when distilled with water, showing that the amygdaline is really the source of the essence. Again, if boiling water be poured over the bitter almond cake, no essential oil is produced, even when the mixture is allowed to stand for some time, but if to this mixture there be added an emulsion of sweet almonds prepared with cold water, the bitter almond oil is at once formed, which is not the case, however, if the emulsion be prepared with boiling water.

From this it is evident that a substance exists in both sweet and bitter almonds which is capable of developing the essence from the amygdaline contained in the latter, but which loses its power when acted upon by hot water. This may be still further proved by dissolving pure amygdaline in water, and adding an emulsion of sweet almonds, when the essence is at once produced.

When the emulsion of sweet almonds is filtered and mixed with alcohol, a white substance resembling albumen is precipitated, which contains carbon, hydrogen, nitrogen, and oxygen, and very easily putrefies when exposed to the air in a moist state. If this substance, which is called *emulsine* or *synaptase* (*συνάπτω, to bring into action*), be dissolved in cold water, and mixed with a solution of amygdaline, the oil of bitter almonds is soon formed in abundance, but if the solution of emulsine be boiled, it is no longer capable of developing the essence. On examining the solution of amygdaline in which the essential oil has been produced by the action of emulsine, it is found to contain, in addition, hydrocyanic acid (CHN), grape-sugar ($C_6H_{14}O_7$), and formic acid (CH_2O_2), so that the decomposition may be thus represented—



$$2C_{20}H_{27}NO_{11} = 4C_7H_6O + 2CHN + C_6H_{14}O_7 + 4CH_2O_2 + 3H_2O.$$

The formation of the essential oil of bitter almonds must be regarded, therefore, as dependent upon a species of fermentation or metamorphosis of the bitter principle amygdaline, induced by contact with an albuminous substance, emulsine, itself very prone to undergo decomposition when exposed to air in the presence of moisture.

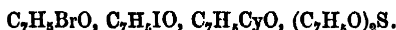
This essential oil may also be obtained from laurel leaves, and from the kernels of most stone fruit.

When the oil of bitter almonds is distilled over, it is accompanied by the hydrocyanic acid formed at the same time, and it is this which renders the ordinary commercial oil so powerful a poison, for if it be purified by distillation from a mixture of lime and chloride of iron (see *Prussian blue*), which retains the hydrocyanic acid, it becomes comparatively harmless. A better process for obtaining the pure oil of bitter almonds consists in shaking the crude oil with an equal volume of a strong solution of bisulphite of soda, with which it forms a white crystalline compound. If this be distilled with solution of carbonate of soda, the pure oil passes over.

The poisonous properties of laurel-water, and similar preparations, are also due to the presence of hydrocyanic acid.

The crude essential oil of bitter almonds also contains a crystalline substance called *benzoine* ($C_{14}H_{12}O_2$), which is interesting as being polymeric with the essence, into which it may be converted by passing its vapour through a red-hot tube. The crude oil may be entirely converted into this substance by shaking it with an alcoholic solution of potash.

When the pure essential oil of bitter almonds (C_7H_6O) is acted upon by dry chlorine, it evolves hydrochloric acid, and becomes converted into a colourless liquid, having an odour of horse-radish, and containing C_7H_5ClO, an atom of hydrogen having been removed, and its place filled by an atom of chlorine. If this liquid be acted upon by the bromides, iodides, cyanides, or sulphides of the metals, the chlorine is removed in its turn, the vacancy being filled up by bromine, iodine, cyanogen or sulphur, compounds being obtained which have the formulæ—



$$C_7H_5BrO,\ C_7H_5IO,\ C_7H_5CyO,\ (C_7H_5O)_2S.$$

When boiled with water, this chlorine compound is converted into benzoic acid—



$$C_7H_5ClO + H_2O = C_7H_5O_2.H + HCl.$$

On comparing the composition of these compounds with that of the essential oil from which they are derived, our attention is called to the existence of C_7H_5O in all of them—

Oil of bitter almonds, .	$(C_7H_5O)H$
Benzoic acid, . . .	$(C_7H_5O)HO$
Chlorine compound, .	$(C_7H_5O)Cl$
Bromine ,, . .	$(C_7H_5O)Br$, &c.

This circumstance led many chemists to assume the existence in these compounds of the radical *benzoyle* (C_7H_5O), capable of playing the part of an elementary substance in uniting with oxygen, chlorine, &c., and therefore resembling the elements in its chemical tendencies, from which resemblance it is spoken of as a quasi-element or compound radical.

If this radical be represented by Bz, the formation of the members of the *benzoyle series* from oil of bitter almonds will be simply and easily traced.

Oil of bitter almonds, *hydride of benzoyle*, .	BzH
Benzoic acid, *benzoyle hydrate*, . . .	BzHO
Chloride of benzoyle, ...	BzCl
Bromide ,, ...	BzBr
Iodide ,, ...	BzI
Cyanide ,, ...	BzCy
Sulphide ,, ...	Bz_2S

The radical benzoyle itself has been recently obtained in a separate state by the action of sodium on chloride of benzoyle. It forms prismatic crystals, which fuse easily, and may be sublimed without decomposition. They are sparingly soluble in alcohol and ether. The formula C_7H_5O should be doubled to express correctly a molecule of this radical (see *Alcohol radicals*).

It will be noticed that *benzoic anhydride* is not included in the above enumeration of the benzoyle series. This compound, which may be represented as Bz_2O, or $(C_7H_5)_2O$, is obtained by heating benzoate of soda with chloride of benzoyle—

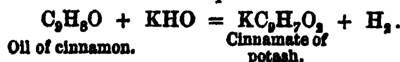


$$NaBzO + BzCl = NaCl + Bz_2O.$$

This substance has no acid properties whatever. It does not dissolve in cold water, but if boiled with water, is slowly converted into benzoic acid.

When oil of bitter almonds is decomposed by hydrate of potash dissolved in alcohol, it yields *benzoic alcohol* (C_7H_8O), which will be more particularly noticed hereafter.

341. Very closely connected with the essential oil of bitter almonds are the essences of cinnamon and cassia, which consist chiefly of an oxidised essence, represented by the formula C_9H_8O, and convertible by boiling with nitric acid into the essence of almonds. By heating the essence of cinnamon with hydrate of potash, it is oxidised and converted into cinnamate of potash—



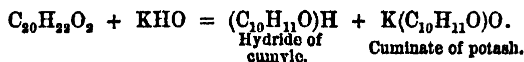
$$C_9H_8O + KHO = KC_9H_7O_2 + H_2.$$

Oil of cinnamon. Cinnamate of potash.

On dissolving this salt in water, and adding an acid, the *cinnamic acid* is precipitated in feathery flakes, closely resembling benzoic acid, both in appearance and chemical characters.*

The same reasons exist as in the case of the benzoyle series, for assuming the existence in the compounds derived from oil of cinnamon of the radical *cinnamyle*, C_9H_7O, so that the oil of cinnamon would be a hydride of cinnamyle $(C_9H_7O)H$, and cinnamic acid the cinnamyle hydrate $(C_9H_7O)HO$.

Essential oil of cummin is a mixture of the hydrocarbon cymole ($C_{10}H_{14}$), which has been already noticed, with an oxidised essence, $C_{10}H_{12}O$, which is closely analogous to those of almonds and cinnamon, and is called *hydride of cumyle* $(C_{10}H_{11}O)H$; when acted upon by oxidising agents it yields *cuminic acid* ($HC_{10}H_{11}O_2$), which resembles benzoic acid, but is characterised by an odour similar to that of the bug. From the hydride of cumyle an oily compound has been obtained, which is polymeric with the supposed radical *cumyle*, having the composition $C_{20}H_{22}O_2$, and that it is really composed of a double molecule of that radical is rendered very probable by its behaviour when fused with hydrate of potash, its hydrogen converting one molecule of cumyle into hydride of cumyle, whilst its oxygen converts the other into cuminic acid—



$$C_{20}H_{22}O_2 + KHO = (C_{10}H_{11}O)H + K(C_{10}H_{11}O)O.$$

Hydride of cumyle. Cuminate of potash.

The essential oils of *aniseed, fennel,* and *tarragon* contain, in addition to a hydrocarbon isomeric with turpentine, a solid crystalline oxidised essence ($C_{10}H_{12}O$) isomeric with the hydride of cumyle. That this substance is not hydride of cumyle, however, is at once proved by the action of oxidising agents, which convert it into *hydride of anisyle* $(C_8H_7O_2)H$, and *anisic acid*, $HC_8H_7O_3$, the latter being isomeric with winter-green oil (see p. 462).

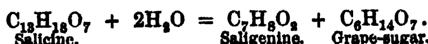
342. Salicine and its derivatives—Glucosides.— *Oil of spiræa*, or *meadow sweet*, consists chiefly of the compound ($C_7H_6O_2$) isomeric with benzoic acid; this compound is easily obtained artificially by the oxidation of *salicine*, a bitter substance extracted from willow bark, by boiling it in water, removing the colouring matter and tannin from the solution by boiling with hydrated oxide of lead, precipitating the excess of lead by hydrosulphuric acid, and evaporating the filtered liquid, when the salicine crystallises out, and may be obtained by recrystallising from alcohol, in beautiful white needles having the composition $C_{13}H_{18}O_7$.

Salicine is sparingly soluble in cold water and insoluble in ether, but dissolves readily in boiling water and in alcohol. It is readily distinguished by the red colour which it gives with concentrated sulphuric acid, which manifests its presence when applied to the inner bark of the willow. When distilled with dilute sulphuric acid and bichromate of potash, it yields the oil of spiræa.

The changes suffered by salicine when boiled with a dilute mineral acid (as sulphuric) are very remarkable, for after the boiling has been continued for a few

* Oil of bitter almonds has been converted into cinnamic acid by heating it with acetic oxychloride; $C_7H_6O + (C_2H_3O)Cl = C_7H_5(C_2H_3O)O + HCl$.

minutes, the solution is found to contain grape-sugar, together with a crystalline substance called *saligenine*, which is distinguished by the intense blue colour which it gives with perchloride of iron. The change is easily explained, for the addition of 2 molecules of water to salicine would provide the elements of grape-sugar and saligenine—



$$C_{13}H_{18}O_7 + 2H_2O = C_7H_8O_2 + C_6H_{14}O_7.$$

Salicine. Saligenine. Grape-sugar.

Emulsine or synaptase is capable of effecting this change in salicine, and it will be remembered that grape-sugar is one of the products of the action of that ferment upon amygdaline. If the ebullition of the diluted acid be continued for a length of time, the liquid deposits a resinous substance, *saliretine*, which is isomeric with oil of bitter almonds (C_7H_6O).

A very striking example of the stability of types, notwithstanding the substitution of one element for another, is found in the circumstance that salicine, under the influence of chlorine, yields three different products containing chlorine in place of hydrogen, and that when these are boiled with dilute acids, they yield other products containing chlorine, and bearing the same relation to their chlorinated primitive which saligenine and saliretine respectively bear to salicine.

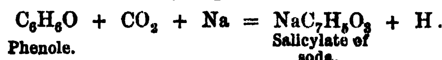
Thus we have—

Salicine, ...	$C_{13}H_{18}\ O_7$	Saligenine, ...	$C_7H_8\ O_2$
Chlorosalicine, . .	$C_{13}\begin{matrix}H_{17}\\Cl\end{matrix}\Big\}O_7$	Chlorosaligenine, . .	$C_7\begin{matrix}H_7\\Cl\end{matrix}\Big\}O_2$
Dichlorosalicine, .	$C_{13}\begin{matrix}H_{16}\\Cl_2\end{matrix}\Big\}O_7$	Dichlorosaligenine, .	$C_7\begin{matrix}H_6\\Cl_2\end{matrix}\Big\}O_2$
Trichlorosalicine, .	$C_{13}\begin{matrix}H_{15}\\Cl_3\end{matrix}\Big\}O_7$	Trichlorosaligenine, .	$C_7\begin{matrix}H_5\\Cl_3\end{matrix}\Big\}O_2$

When salicine is fused with hydrate of potash, the mass dissolved in water, and hydrochloric acid added, beautiful needles of *salicylic acid* ($HC_7H_5O_3$) are separated. This acid may also be obtained from the oil of spiræa by a similar process, and it will be seen that salicylic acid bears the same relation to this oil as benzoic acid bears to oil of bitter almonds—

Oil of bitter almonds,	C_7H_6O	Oil of spiræa, . . .	$C_7H_6O_2$
Benzoic acid, . .	$C_7H_6O_2$	Salicylic acid, . . .	$C_7H_6O_3$.

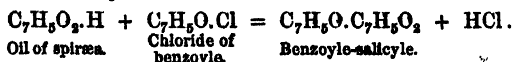
Salicylic acid has been obtained in a most interesting manner by the simultaneous action of carbonic acid and sodium upon phenole—



$$C_6H_6O + CO_2 + Na = NaC_7H_5O_3 + H.$$

Phenole. Salicylate of soda.

Exactly as chemists have been led to consider the bitter almond oil as hydride of benzoyle, so they have regarded oil of spiræa as *hydride of salicyle* ($C_7H_5O_2.H$), assuming the existence of the radical *salicyle* (C_7H_5O), of which salicylic acid would be the hydrate. We find this view of the constitution of these compounds supported by the circumstance, that when the oil of spiræa is heated with chloride of benzoyle, a substance is obtained which may be regarded as composed of the two radicals salicyle and benzoyle—



$$C_7H_5O_2.H + C_7H_5O.Cl = C_7H_5O.C_7H_5O_2 + HCl.$$

Oil of spiræa. Chloride of benzoyle. Benzoyle-salicyle.

From a careful study of the behaviour of salicine under the action of various re-agents, the inference has been drawn that it is a compound of saligenine ($C_7H_8O_2$) with a substance ($C_6H_{10}O_5$), which becomes converted into grape-sugar, by assimilation of water, as soon as it is separated from the saligenine.

Salicine is occasionally employed in medicine as a febrifuge, and is a common adulteration of quinine.

Salicine is the chief member of the class of substances termed *glucosides*, from the presence of grape-sugar (glucose) among their products of decomposition. To this class belong several other substances much resembling salicine, and, like it, extracted from the barks of different trees.

343. *Populine* ($C_{20}H_{22}O_8$) is a sweet crystalline substance obtained from the bark and leaves of the aspen, and especially interesting from its close connection with the benzoyle and salicyle series; for when boiled with solution of baryta, it is decomposed into benzoic acid (which unites with the baryta) and salicine—



$$\underset{\text{Populine.}}{2C_{20}H_{22}O_8} + BaO.H_2O = \underset{\text{Benzoate of baryta.}}{Ba(C_7H_5O_2)_2} + \underset{\text{Salicine.}}{2C_{13}H_{18}O_7}.$$

Nor is this the only connecting link, for populine yields oil of spiræa when distilled with sulphuric acid and bichromate of potash, and when boiled with dilute acids it furnishes benzoic acid, saliretine, and grape-sugar—



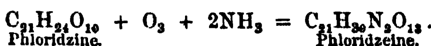
$$\underset{\text{Populine.}}{C_{20}H_{22}O_8} + 2H_2O = \underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Saliretine.}}{C_7H_6O} + \underset{\text{Grape-sugar.}}{C_6H_{14}O_7}.$$

In order to explain this production of benzoyle and salicyle compounds from populine, it is usual to regard this substance as formed from salicine ($C_{13}H_{18}O_7$) by the introduction of a molecule of benzoyle (C_7H_5O), in the place of an atom of hydrogen—



$$\underset{\text{Populine.}}{C_{20}H_{22}O_8} = \underset{\text{Benzoyle-salicine.}}{C_{13}H_{17}(C_7H_5O)O_7}.$$

Phloridzine ($C_{21}H_{24}O_{10}$) is extracted from the bark of the apple, pear, plum, and cherry tree; it crystallises readily, is slightly bitter, and when boiled with dilute acids, yields grape-sugar and a resinous substance called *phloretine* ($C_{15}H_{14}O_5$). Its most interesting property is that of forming a red compound (*phloridzeine*) when exposed to the joint influences of air and ammonia—

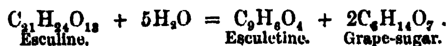


$$\underset{\text{Phloridzine.}}{C_{21}H_{24}O_{10}} + O_3 + 2NH_3 = \underset{\text{Phloridzeine.}}{C_{21}H_{30}N_2O_{13}}.$$

This red compound combines with ammonia to form a purple mass with a coppery lustre, which dissolves in water with a fine blue colour. The production of this colouring matter from phloridzine is an excellent example of that conjoined action of air and ammonia by which certain natural colouring matters, such as litmus, are formed from substances which are themselves destitute of colour.

Quercitrine ($C_{33}H_{30}O_{17}$) is the yellow colouring matter extracted by alcohol from the bark of the quercitron. It is a crystallisable substance, and is decomposed by boiling with acids into grape-sugar and a yellow crystalline body called *querceline* ($C_{27}H_{18}O_{12}$).

Esculine ($C_{21}H_{24}O_{13}$) is extracted from the bark of the horse-chestnut by boiling water. If the tannin and colouring matter be precipitated from the infusion by acetate of lead, the filtered liquid treated with sulphuretted hydrogen to remove the excess of lead, and the solution, after a second filtration, evaporated, the esculine is obtained in colourless needles. It is remarkable for its *fluorescence*; although its solution is colourless by transmitted light, it appears of a beautiful deep blue colour when viewed at certain angles. This substance is also a glucoside, for when boiled with dilute acids, it yields grape-sugar and a crystalline substance known as *esculetine*.



$$\underset{\text{Esculine.}}{C_{21}H_{24}O_{13}} + 5H_2O = \underset{\text{Esculetine.}}{C_9H_6O_4} + \underset{\text{Grape-sugar.}}{2C_6H_{14}O_7}.$$

Paviine also occurs in the horse-chestnut bark, but in far larger quantity in the bark of the ash. It is distinguished from esculine by exhibiting a green fluorescence.

Saponine is a substance closely allied to the glucosides, and is found in the soapwort, the fruit of the horse-chestnut, the pimpernel, the root of the pink, and in many other plants. It may be extracted by boiling alcohol, which deposits it in an amorphous state on cooling. Saponine is soluble in water, and its solution is characterised by the readiness with which it lathers, like soap and water, although it may contain a very small quantity of saponine. This property leads to the use of decoctions containing it, such as those of the soap-wort, and of the soap-nut of India, for the purpose of cleansing certain delicate fabrics.

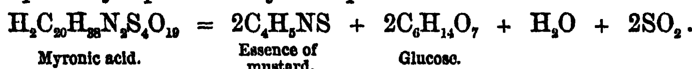
Picrotoxine ($C_5H_6O_2$) is a crystalline substance, to which the poisonous properties of *Cocculus indicus* are due. It appears to have feeble acid tendencies, and is extracted from an acidified solution by shaking with ether. On evaporating the ethereal solution it leaves prismatic needles of an intensely bitter taste.

344. **Essential oils containing sulphur—Allyle series.**—The essential oils of *asafœtida*, of *cress*, *garlic*, *horseradish*, *leeks*, *mustard*, *onions*,

and *radishes*, differ from those which have been already described by containing sulphur.

Those of asafœtida, cress, garlic, leeks, onions, and radishes, are composed essentially of the same substance, represented by the formula $C_6H_{10}S$. The essence of mustard and that of horseradish are composed of C_4H_5NS.

The chemistry of the origin of essential oil of mustard is analogous to that of essence of almonds. The oil is obtained from the seeds of the black mustard after removing the fixed oil (which has no pungency whatever) by pressure; on moistening the crushed seed with water, the production of the essential oil is indicated by its peculiar odour, and it may be separated from the seeds by distillation. The mustard seeds contain a salt of potash with a peculiar acid called *myronic acid*,* ($H_2C_{20}H_{38}N_2S_4O_{19}$), together with a substance similar to the emulsine of almonds, which has been termed *myrosine*, and is capable of inducing the decomposition of the myronic acid, and the consequent production of essence of mustard, just as the emulsine of almonds developes the essential oil by the decomposition of the amygdaline; in the case of mustard, however, the nature of the decomposition has not been so clearly made out, but is probably represented by the equation—

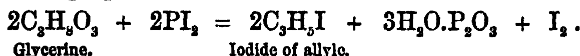


$$H_2C_{20}H_{38}N_2S_4O_{19} = 2C_4H_5NS + 2C_6H_{14}O_7 + H_2O + 2SO_2.$$

Myronic acid. Essence of mustard. Glucose.

The essence of mustard has been produced artificially in a very interesting and remarkable manner,

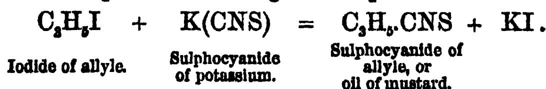
When glycerine (the sweet principle of the fats and fixed oils) is distilled with the biniodide of phosphorus, a colourless ethereal liquid is obtained, which has the composition C_3H_5I, and is called *iodide of allyle*, because when distilled with sodium, it yields iodide of sodium and a volatile liquid composed of C_3H_5, and called *allyle*, in allusion to its peculiar odour (*allium, garlic*). The formation of iodide of allyle is explained by the following equation—



$$2C_3H_8O_3 + 2PI_2 = 2C_3H_5I + 3H_2O.P_2O_3 + I_2.$$

Glycerine. Iodide of allyle.

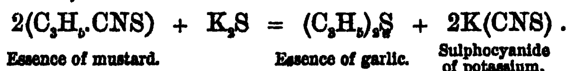
When iodide of allyle is distilled with sulphocyanide of potassium, an oily liquid is obtained, identical in properties and composition with oil of mustard, which must therefore be regarded as a *sulphocyanide of allyle*, its artificial production being thus explained—



$$C_3H_5I + K(CNS) = C_3H_5.CNS + KI.$$

Iodide of allyle. Sulphocyanide of potassium. Sulphocyanide of allyle, or oil of mustard.

Additional interest is created in this artificial formation of oil of mustard when it is found to be convertible into oil of garlic, by being heated with sulphide of potassium, when sulphocyanide of potassium is formed at the same time, thus—



$$2(C_3H_5.CNS) + K_2S = (C_3H_5)_2S + 2K(CNS).$$

Essence of mustard. Essence of garlic. Sulphocyanide of potassium.

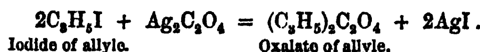
Hence it is inferred that the essence of garlic is a *sulphide of allyle*, of which essence of mustard is a sulphocyanide.

* From μύρον, an unguent.

The oil of *Cochlearia officinalis* is sometimes sold as essential oil of mustard, which it much resembles; but the former is sulphocyanide of butyle $C_4H_9.CNS$, and boils at 160° C., whilst the latter boils at 147° C.

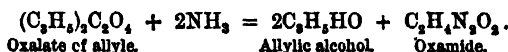
A considerable number of compounds are included in the *allyle series*, but are not at present possessed of any practical importance.

The *allylic alcohol* (C_3H_5HO) is interesting as the prototype of a new class of alcohols, parallel with that represented by common alcohol (C_2H_5HO). In order to obtain it, the iodide of allyle is decomposed by oxalate of silver, when oxalate of allyle is obtained—



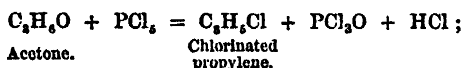
$$\underset{\text{Iodide of allyle.}}{2C_3H_5I} + Ag_2C_2O_4 = \underset{\text{Oxalate of allyle.}}{(C_3H_5)_2C_2O_4} + 2AgI.$$

By treating oxalate of allyle with ammonia, allylic alcohol and oxamide are obtained—

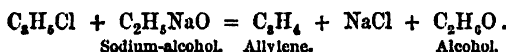


$$\underset{\text{Oxalate of allyle.}}{(C_3H_5)_2C_2O_4} + 2NH_3 = \underset{\text{Allylic alcohol.}}{2C_3H_5HO} + \underset{\text{Oxamide.}}{C_2H_4N_2O_2}.$$

Allylene (C_3H_4), the olefiant gas of the allyle series, is homologous with acetylene (C_2H_2), and much resembles it in its chemical relations. It has been prepared by heating chlorinated propylene in a sealed tube with sodium-alcohol. The chlorinated propylene is a product of the action of pentachloride of phosphorus upon acetone—



$$\underset{\text{Acetone.}}{C_3H_6O} + PCl_5 = \underset{\text{Chlorinated propylene.}}{C_3H_5Cl} + PCl_3O + HCl;$$



$$C_3H_5Cl + \underset{\text{Sodium-alcohol.}}{C_2H_5NaO} = \underset{\text{Allylene.}}{C_3H_4} + NaCl + \underset{\text{Alcohol.}}{C_2H_6O}.$$

By its action on ammoniacal nitrate of silver, it yields *argentallylene*, C_3H_3Ag. When sodium is heated in allylene, carbon and hydrogen are liberated, and sodic acetylide is formed, $C_3H_4 + Na_2 = C_2Na_2 + C + H_4$, a little propylene ($C_3H_6$) is formed at the same time.

345. GUM-RESINS.—The *gum-resins* consist of a mixture of gum with resin, and occasionally with essential oil, and are distinguished by their behaviour when triturated with water, which dissolves the gum and leaves the oil and resin suspended, giving the liquid a milky appearance. They also differ from most resins in being only partially soluble in alcohol. The gum-resins exude from the plants producing them in a milky state, gradually solidifying by exposure to the air.

Asafœtida contains a resin of the composition $C_{20}H_{26}O_5$, and owes its powerful odour to an essential oil containing sulphur, which has been already noticed. *Galbanum, ammoniacum, aloes, olibanum* or *frankincense, scammony, gamboge, myrrh,* and *euphorbium,* also belong to the class of gum-resins.

Caoutchouc (C_5H_8) is so far allied to the gum-resins, that it is procured from a milky exudation furnished by several tropical plants, particularly by the *Hævœa guianensis* and *Jatropha elastica.* Incisions are made in these trees, and the milky liquid thus obtained is spread upon a clay bottle-shaped mould, which is then suspended over a fire; a layer of caoutchouc is thus deposited upon the mould, and its thickness is afterwards increased by repeated applications of the milky liquid, the mould being eventually broken out of the caoutchouc bottle thus formed. The dark colour of the caoutchouc found in commerce is believed to be due to the smoke from the fire over which it is dried, for pure caoutchouc is white, and may be obtained in this state by dissolving in washed ether

and precipitating it by the addition of alcohol, in which it is insoluble. The caoutchouc of commerce contains a small quantity of albumen, derived from the original milky liquid, this being really a solution of albumen holding in suspension about 30 per cent. of caoutchouc, which rises to the surface like cream, when the juice is diluted with water and allowed to stand, becoming coherent and elastic when exposed to air. It will be remembered that many of the chief uses of caoutchouc depend upon its physical rather than its chemical properties, its lightness (sp. gr. 0·93) and impermeability to water adapting it for the fabrication of waterproof articles of clothing, of life-buoys, &c., whilst its remarkable elasticity gives rise to a still greater variety of applications.

For the manufacture of waterproof cloth, caoutchouc is dissolved in rectified turpentine, and the solution is spread, in a viscid state, over the surfaces of two pieces of cloth of the same size, which are then laid face to face and passed between rollers, the pressure of which causes perfect adhesion between the two surfaces. Bisulphide of carbon, benzole, and coal naphtha, petroleum, the oils, both fixed and volatile, are also capable of dissolving caoutchouc.

Marine glue is a solution of caoutchouc with a little shell-lac in coal tar naphtha.

Waterproof felt is made by matting together fibres of cotton impregnated with a solution of caoutchouc in naphtha, and passing the felt between rollers. When kept for a length of time, its strength and waterproof qualities are deteriorated, in consequence of the oxidation of the caoutchouc, which is thus converted into a resinous substance resembling shell-lac, and easily dissolved by alcohol.

The alkalies and diluted acids are without effect upon caoutchouc. When gently warmed, it becomes far more soft and pliable; it fuses at about 250° F., and is converted into an oily liquid which becomes viscid on cooling, but will not again solidify, and is useful for lubricating stopcocks. When further heated in air, it burns with a bright smoky flame. Heated in a retort, caoutchouc is decomposed into several hydrocarbons, one of which, called *isoprene*, boils at about 100° F., and has the composition C_5H_8, while *caoutchine* has the same composition as oil of turpentine, and boils at 340° F.; they are well adapted for dissolving caoutchouc.

Vulcanised caoutchouc is produced by incorporating this substance with 2 or 3 per cent. of sulphur, which not only increases in a remarkable manner its elasticity, but prevents it from cohering under pressure, and from adhering to other surfaces unless strongly heated. The vulcanised caoutchouc is also insoluble in turpentine and naphtha. Ordinary vulcanised caoutchouc generally contains more sulphur than is stated above, which causes it to become inelastic and brittle after it has been some time in use; and for some purposes, such as the manufacture of overshoes, it is found advantageous to add some carbonate of lead as well as sulphur.

When a sheet of caoutchouc is allowed to remain for some time in fused sulphur at 250° F., it absorbs 12 or 15 per cent. of that element without suffering any material alteration; but if it be heated for a short time to 300° F., it becomes vulcanised; and when still further heated, is converted into the black horny substance called *vulcanite* or *ebonite*, and used for the manufacture of combs, &c. By treating the vulcanised caoutchouc with sulphite of soda, the excess of sulphur above 2 or 3 per cent. may be dissolved out. The whole of the sulphur may be removed, and the caout-

chouc devulcanised, by boiling it with a 10 per cent. solution of caustic soda.

There are several processes employed for the manufacture of vulcanised caoutchouc; sometimes the sulphur is simply incorporated with it by mechanical means. Another process consists in immersing the caoutchouc in a mixture of 100 parts of bisulphide of carbon with 2·5 parts of chloride of sulphur (S_2Cl_2),* or in dissolving the sulphur in oil of turpentine, which is afterwards used to dissolve the caoutchouc; when the turpentine has evaporated, a mixture of caoutchouc and sulphur is left, which may easily be moulded into any desired form, and afterwards vulcanised by exposure to high pressure steam having a temperature of about 280° F.

The true chemical constitution of vulcanised caoutchouc is not yet understood; it has been suggested that the sulphur has been substituted for a portion of the hydrogen in the original caoutchouc, but it does not seem improbable that this hydrocarbon may combine directly with sulphur.

Caoutchouc is by no means rare in the vegetable world, being found in the milky juices of the poppy (and thence in opium), of the lettuce, and of the euphorbium and asclepia families.

Gutta percha, like caoutchouc, is originally a milky juice which exudes from incisions made into the wood of the *Isonandra percha*, a native of the Eastern archipelago. This juice soon solidifies when exposed to air, to a brownish mass heavier than caoutchouc (sp. gr. 0·98), and differing widely from it by being tough and inelastic at the ordinary temperature, becoming quite soft and plastic when heated nearly to the boiling point of water. Being impervious to water, it is employed as a waterproof material and for water-pipes, whilst its want of conducting power for electricity is turned to account in the coating of wires for the electric telegraph.

Gutta percha is dissolved by the same substances which dissolve caoutchouc. It dissolves very slowly in ether, but is not affected by diluted acids and alkalies, and is employed for the manufacture of bottles in which hydrofluoric acid is kept. It liquefies at a moderately high temperature, and is afterwards decomposed, yielding products similar to those obtained from caoutchouc.

The gutta percha of commerce appears to contain only about 80 per cent. of pure gutta percha ($C_{20}H_{32}$), which is soluble in ether, the remainder consisting of two resins which may be dissolved out by boiling with alcohol, when a white crystalline resin ($C_{20}H_{32}O_2$) is deposited on cooling, leaving an amorphous resin ($C_{20}H_{32}O$) in solution.

Pure gutta percha, exposed to air, is gradually converted into these resinous bodies, unless light be excluded.

346. Gums.—Connected with the substances just described as being immediate products of vegetable life, are the *gums*, which, though resembling the resins in transparency and lustre, are at once distinguished from them by their solubility or softening in water, and by their insolubility in alcohol.

Gum arabic, which may be studied as the representative of this class, is an exudation from certain species of acacia, and consists essentially of *arabine*, which has the composition $C_{12}H_{22}O_{11}$. It dissolves readily, even in cold water, in large proportion, forming a viscid liquid, from which the arabine is precipitated in white flakes on adding alcohol.

* A mixture of sulphur and chloride of lime is said to be sometimes employed.

When arabine is boiled with diluted sulphuric acid, it is converted slowly into grape-sugar ($C_6H_{14}O_7$) by assimilating the elements of water, a property connecting it closely with starch, which is susceptible of a similar conversion.

But a chemical property distinguishing the gums is their behaviour with nitric acid, which furnishes *mucic acid* ($H_2C_6H_8O_8$) and oxalic acid ($H_2C_2O_4$). The latter acid is also formed by the action of nitric acid upon starch and sugar, whilst mucic acid may be obtained by a similar process from sugar of milk and from manna sugar (mannite).

Gum senegal is often used in place of gum arabic, especially by calico-printers to thicken their colours. It is darker in colour than gum arabic, but also consists essentially of arabine.

Gum tragacanth ($C_{12}H_{20}O_{10}$), which exudes from the *Astragalus tragacantha*, is far less transparent than gum arabic, from which it also differs by not dissolving in water, but merely swelling up to a soft gelatinous mass. This variety of gum, which is also called *mucilage, cerasine*, or *bassorine*, is found, together with arabine, in the gum which exudes from the cherry, plum, almond, and apricot trees, and gives the mucilaginous character to the watery decoctions prepared from certain seeds, such as linseed and quince-seed, and from the root of the marsh-mallow.

STARCH.

347. Starch ($C_6H_{10}O_5$) differs widely from the vegetable products just noticed, in being an indispensable constituent of certain parts of plants, in possessing an organised structure, and playing a very important part in the nutrition of the plant.

In composition, it is seen to correspond with cellulose, which has also, it will be remembered, an organised structure; but the function of cellulose in the plant appears to be chiefly, if not entirely, a mechanical one, since it forms the skeleton or framework of the plant, for which its resistance to chemical change especially adapts it; whilst it will be seen that starch suffers chemical changes in the vegetable, which may be compared in some measure to the digestion of the food in the animal body.

Starch is manufactured chiefly from potatoes, wheat, and rice.

The solid portion of the potato consists chiefly of starch, as appears in the following result of analysis :—

Composition of the Potato.

Water,	75·9
Vegetable albumen,	2·3
Oily matter,	0·2
Woody fibre,	0·4
Starch,	20·2
Mineral substances,	1·0
	100·0

In order to extract the starch, the potatoes are rasped to a pulp, which is washed upon a sieve, under a stream of water, as long as the latter is rendered milky by the starch suspended in it, the woody fibre being left behind upon the sieve. The milky liquid is allowed to settle, and the clear water drawn off; the deposited starch is then stirred up with fresh water, and again allowed to subside, this process being repeated as long as the water is coloured, after which the starch is mixed with a small

quantity of water, and passed through a fine sieve to separate mechanically mixed impurities; it is finally drained and dried, first, in a current of air, and afterwards by a gentle heat.

Starch cannot be extracted from wheat so easily as from potatoes, on account of the much larger proportion of other solid matters from which it must be separated.

Composition of Wheat.

Water,	12·1
Vegetable albumen,	2·0
Oily matter,	1·1
Woody fibre,	1·5
Starch,	60·8
Dextrine and sugar,*	10·5
Gluten,	10·5
Mineral substances,	1·5
	100·0

To extract the starch, the coarsely-ground wheat is moistened with water, and allowed to putrefy, as it easily does, in consequence of the alterable character of the gluten (which contains carbon, hydrogen, nitrogen, oxygen, and sulphur); the putrefying gluten excites fermentation in the sugar and part of the starch, producing acetic and lactic acids. These acids are capable of dissolving the remainder of the gluten, which may then be washed away by water, the subsequent processes being similar to those employed in the extraction of potato starch.

A far more economical and scientific method of extracting the starch consists in dissolving the gluten by means of a weak alkaline solution, which leaves the starch untouched. This process is especially applied in the manufacture of starch from rice, the composition of which is here given:—

Composition of Rice.

Water,	5·0
Starch,	83·0
Gluten,	6·0
Woody fibre,	4·8
Sugar, Dextrine,	1·0
Oily matter,	0·1
Mineral matters,	0·1
	100·0

The whole rice is allowed to soak for twenty-four hours in water containing $\frac{1}{350}$th of its weight of caustic soda; it is then washed and ground into flour, which is again soaked for two or three days in a fresh alkaline solution; the starch is allowed to settle, and the alkaline liquor holding the gluten in solution is drawn off. To complete the purification of the starch, it is stirred up with water, the heavier woody fibre allowed to subside, and the milky liquid is run off into another vessel, where it deposits the starch.

Starch is usually sent into commerce in the rough prismatic fragments into which it splits during the process of drying, and is generally coloured blue by the addition of a little artificial ultramarine or smalt, in order to correct the yellow tint of linen. Commercial starch generally contains about 18 per cent. of water.

* The existence of sugar in wheat is denied by Péligot.

Starch being possessed of an organised structure, might be expected to vary in external characters with the source from which it was derived; and, accordingly, we find that, with the help of the microscope, it may be ascertained from what plant any particular specimen of starch was procured, a result which could not be arrived at by a chemical examination.

Thus, powdered starch from the potato (P, fig. 288) appears under the microscope in very irregular ovoid granules, marked with concentric rings, and of larger size than those from most other vegetables, the long diameter

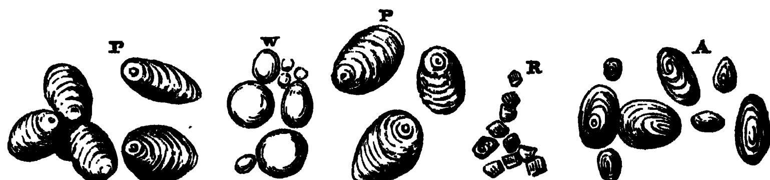


Fig. 288.

of the grains being usually about $\frac{1}{300}$ inch. Wheat starch (W) exhibits grains which are nearly circular, and are not marked with rings; they are much smaller than those of potato starch, having a diameter of about $\frac{1}{1000}$ of an inch. The grains of rice starch (R) are angular, and still smaller, measuring only about $\frac{1}{3000}$ of an inch in diameter. A represents the starch granules of arrow-root.

Starch is quite unaffected by cold water; but if it be heated with water to a temperature above 140° F., the granules swell up, burst, and yield the well-known viscid liquid used by laundresses. If this be mixed with a large quantity of water, and allowed to stand, some of the imperfectly burst granules subside, but the greater part of the starch remains so intimately mixed with the water, that it is not separated by filtration through paper, though it has been shown that when the rootlets of a hyacinth are immersed in the diluted magma of starch, the water alone is taken up by the capillary vessels, affording a strong presumption that the starch was simply in a state of suspension in the water. If the boiled starch be evaporated to dryness, a brittle mass remains, which may again be taken up without difficulty by water.

This peculiar behaviour of starch with water is closely connected with its use as food. Raw starch is digested with difficulty, and often passes unaltered through the bowels; but the ease with which the starch gelatinised by heat is digested, is shown by the wholesomeness of sago, tapioca, and arrow-root, which consist simply of starch, and are prepared for food by heating them with water to the point at which the granules burst.

Arrow-root is the starch extracted from the root of the *Maranta arundinacea*, and of some other tropical plants.

In the preparation of tapioca and sago, the starch is dried at a temperature above 140° F., so that it loses its ordinary farinaceous appearance and becomes semi-transparent.

Sago is manufactured from the pith of certain species of palm, natives of the East Indian islands. The tree is split so as to expose the pith, which is mixed with water, and the starch having been separated from the woody fibre in the usual manner, is pressed through a perforated metallic plate, which moulds it into small cylinders; these are placed in a

revolving vessel and broken into rough spherical grains, which are steamed upon a sieve, and dried.

Tapioca is obtained from the roots of the *Jatropha manihot*, a native of America. The roots are peeled and subjected to pressure, which squeezes out a juice employed by the Indians to poison their arrows, and containing a deleterious substance which has been named *jatrophine*. When the juice is allowed to stand, it deposits starch, which is well washed, pressed through a colander, and dried at 212° F.

Oswego, or corn-flour, is the flour of Indian corn deprived of gluten by treatment with a weak solution of soda.

348. *Dextrine*.—When starch is heated in an oven to about 400° F. for an hour or two, it becomes easily soluble in cold water, yielding a solution having all the properties of gum; the starch has indeed been converted into a new substance known as *dextrine* or *British gum*, which is largely used by calico-printers for thickening their colours, and is substituted for ordinary gum in many other applications. There is a current anecdote which attributes the discovery of dextrine to a conflagration at a starch-factory, where the work-people, who assisted in quenching the fire, observed the gummy properties of the water which had been thrown over the torrefied starch. In toasting bread, a portion of the starch is converted into dextrine, which is dissolved by the water in the preparation of toast and water. Farinaceous foods for infants are made by baking flour, in order to convert the starch into dextrine.

It is very remarkable that the composition of dextrine ($C_6H_{10}O_5$) is precisely that of starch; they are *isomeric* bodies, so that the difference in their properties must be ascribed to a difference in the arrangement of their component particles; the name of dextrine was conferred upon this gummy substance on account of the power possessed by its solution of causing a right-handed rotation in a ray of polarised light. When oxidised by nitric acid, dextrine, like starch, is converted into oxalic acid, a circumstance distinguishing it from ordinary gum, which furnishes mucic acid when acted upon by nitric acid.

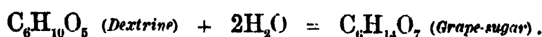
Dextrine is usually prepared on the large scale by moistening 10 parts of starch with 3 parts of water acidulated with $\frac{1}{150}$th of nitric acid; the mixture is allowed to dry, and spread upon trays in an oven, where it is heated for an hour or so to 240° F. The nitric acid thus allows the starch to be converted into dextrine at a temperature which would be quite inadequate to effect the transformation of starch alone.

This power of accelerating the conversion of starch into dextrine is shared by all acids. Hence if starch be boiled with water, and the viscid liquid so obtained be mixed with an acid, and again boiled, it gradually becomes thinner, and is eventually converted into dextrine. The change is very readily effected by boiling the starch solution with a few drops of sulphuric acid, and the gradual conversion of the starch may be traced by means of an aqueous solution of iodine. On adding this solution to a portion of the (cold) solution of starch, it produces the usual dark blue colour; but on adding it, at intervals, to portions of the acidulated and boiled liquid, taken away and cooled for the purpose, the blue colour will be replaced by a peculiar vinous purple tint which iodine imparts to solutions of dextrine containing a little unchanged starch.

The solution of iodine is much used in proximate organic analysis as a test for starch, and it is necessary to bear in mind that the blue colour is

bleached by alkalies (which take up the iodine) and by heat, though, in the latter case, it may be restored by cooling the liquid. The blue colour does not appear to be due to the formation of any definite chemical compound with the starch, but rather to a mechanical adhesion of very finely divided iodine to the particles of starch. The sensitiveness of starch to the action of *free* iodine has given rise to its application in the preparation of paper for the prevention of forgery in bankers' cheques, &c. If paper be impregnated with a mixture of iodide of potassium and starch, which is perfectly white, it will acquire an intense blue colour on the application of any of the bleaching agents (chlorine, hypochlorous acid, chlorides of lime and soda), generally used for removing ink, as these liberate the iodine, which immediately blues the starch.

If the ebullition of the dextrine in contact with the sulphuric acid be continued, the solution entirely loses its property of being coloured by iodine, and acquires a sweet taste, the dextrine having been converted into *glucose* or *grape-sugar* ($C_6H_{14}O_7$) by assimilating the elements of two molecules of water*—

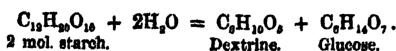


$$C_6H_{10}O_5 \text{ (Dextrine)} + 2H_2O = C_6H_{14}O_7 \text{ (Grape-sugar)}.$$

349. *Germination of seeds—Malting.*—This tendency of starch to combine with the elements of water and pass into grape-sugar, will be found of immense importance in the chemistry of vegetation, as well as in that of food. It is, indeed, the chief chemical change concerned in the development of living from inanimate matter, being one of the first processes involved in the germination of a seed—the first step in the production of vegetables, which must precede the animals whose food they compose.

The components of all seeds are similar to those of wheat, which have been enumerated above; and if they be perfectly dried immediately after their removal from the parent plant, they may be preserved for a great length of time unchanged, and without losing the power of germinating under favourable circumstances. The essential conditions of germination are the presence of air and moisture, and a certain temperature, which varies with the nature of the seed. These conditions being fulfilled, the seed absorbs oxygen from the air, and evolves carbonic acid, produced by the combination of the oxygen with the carbon of one or more of the most alterable constituents of the seed, such as the vegetable albumen or the gluten. This process of oxidation is attended with evolution of heat, which serves to maintain the seed at the degree of warmth most favourable to germination. The component particles of the albumen or gluten having been set in motion by the action of the atmospheric oxygen, induce a movement or chemical change in the starch with which they are in contact, causing it to pass into dextrine and grape-sugar, which, unlike the starch, being perfectly soluble in water, are capable of affording to the developing shoot, the carbon, hydrogen, and oxygen which it requires for the increase of its frame. The production of grape-sugar and of dextrine in germination is well illustrated by the sweet gummy character of the bread made from *sprouted* wheat, and is turned to practical account in the process of malting.

* There is some reason to believe that the formation of grape-sugar from starch results from a change similar to that by which it is obtained from salicine and other glucosides. Thus—



$$\underset{\text{2 mol. starch.}}{C_{12}H_{20}O_{10}} + 2H_2O = \underset{\text{Dextrine.}}{C_6H_{10}O_5} + \underset{\text{Glucose.}}{C_6H_{14}O_7}.$$

During the germination of all seeds there is formed, apparently by the oxidation of one of the more alterable constituents, a peculiar substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained from any other source, and is characterised by its remarkable property of inducing the conversion of starch into dextrine and grape-sugar.

This substance has been termed *diastase* (*διάστασις, dissension; metaph. fermentation*), but has never yet been obtained in a state of sufficient purity to enable its formula to be satisfactorily determined. It may be extracted, however, from malt, by grinding it, and mixing it with half its weight of warm water, which dissolves the diastase; the solution squeezed out of the malt is heated to about 170° F., filtered from any coagulated albumen, and mixed with absolute alcohol, which precipitates the diastase in white flakes. One part of diastase dissolved in water is capable of inducing the conversion of 2000 parts of starch into dextrine and grape-sugar, the diastase itself being exhausted in the process. A temperature of about 150° F. is most favourable to the action of diastase, which may be arrested entirely by raising the liquid to the boiling point.

The great importance of diastase in the arts of the brewer and distiller is at once apparent. In the process of *malting* barley, the grain is soaked in water, and afterwards spread out in thin layers upon the floor of a dark room (thus imitating the natural condition under which the seed germinates), which is maintained as nearly as possible at a constant and moderate temperature (between 55° and 62° F.); spring and autumn are, therefore, more favourable to malting than summer and winter. It soon evolves heat, and the grains begin to swell; in the course of twenty-four hours the germination commences, and the *radicle* makes its first appearance as a whitish protuberance; the grain is turned two or three times a-day, in order to equalise the temperature. In about a fortnight, the radicle has grown to about half an inch, by which time a sufficient quantity of diastase has been formed. In order to prevent the germination from proceeding further, the grain is killed by drying it at a temperature of 90° F. on perforated metallic plates, where it is afterwards heated to about 140° F., so as to render it brittle, after which it is sifted in order to separate the radicle, which is now easily broken off. This radicle is found to contain as much as $\frac{1}{8}$th of the total quantity of the nitrogen present in the barley, so that the *malt dust*, as the siftings are called, forms a valuable manure.

100 parts of barley generally yield about 80 parts of malt, but a part of the loss is due to water present in the barley, so that 100 parts of dry barley yield 90 parts of malt, and 4 parts of malt dust, the difference, viz., 6 parts, representing the weight of the carbon converted into carbonic acid, of the hydrogen (if any) converted into water during the germination, and of soluble matters removed from the barley in steeping. Malt contains about $\frac{1}{500}$th of its weight of diastase, far more than enough to ensure the conversion of the whole of its starch into sugar.

The following table* illustrates the change in composition suffered by barley during the process of malting, leaving the moisture out of consideration :—

* Lawes; Report on the Relative Values of Unmalted and Malted Barley as Food for Stock. 1866.

	Barley.	After Steeping.	14½ days on floor.	Malt after Sifting.	Malt Dust.
Sugar, ...	2·56	1·56	12·14	11·01	11·35
Starch, . . . } Dextrine, . . . }	80·42	81·12	70·09	72·03	43·68
Woody fibre, . .	4·69	5·22	5·03	4·84	9·67
Albuminous matter,	9·83	9·83	10·39	9·95	26·90
Mineral matter, . .	2·50	2·27	2·35	2·17	8·40
	100·00	100·00	100·00	100·00	100·00

350. *Brewing.*—In order to prepare beer, the brewer *mashes* the ground malt with water at about 180° F. for some hours, when the diastase induces the conversion, into dextrine and sugar, of the greater part of the starch which has not been so changed during the germination, and the *wort* is ready to be drawn off for conversion into beer. The undissolved portion of the malt, or *brewers' grains*, still contains a considerable quantity of nitrogenised matter, and is employed for feeding pigs.

That malt contains far more diastase than is necessary to convert its starch into sugar, is shown by adding a little infusion of malt to the viscid solution of starch, and maintaining it at about 150° F. for a few hours, when the mixture will have become far more fluid, and will no longer be coloured blue by solution of iodine. In distilleries, advantage is taken of the excess of diastase in malt, by adding 3 or 4 parts of unmalted grain to it, when the whole of the starch in this latter is also converted into dextrine and sugar, and the labour and expense of malting it are avoided.

The wort obtained by infusing malt in water contains not only grape-sugar, dextrine, and diastase, but a considerable quantity of nitrogenised matter formed from the gluten (or albuminous matter) of the barley. Before subjecting it to fermentation, it is boiled with a quantity of hops, usually amounting to about $\frac{1}{40}$th of the weight of the malt employed, which is found to prevent, in great measure, the tendency of the beer to become sour in consequence of the conversion of the alcohol into acetic acid.

The *hop* contains about 10 per cent. of an aromatic yellow powder, called *lupuline*, which appears to be the active portion, and which contains a volatile oil of peculiar odour, together with a very bitter substance.

The hopped wort is run off into a vat, where it is allowed to deposit the undissolved portion of the hops, and the clear liquor is drawn off into shallow coolers, where its temperature is lowered as rapidly as possible to about 60° F., the cooling being usually hastened by cold water circulating through pipes which traverse the coolers. If the wort be cooled too slowly, the nitrogenised matter which it contains undergoes an alteration by the action of the air, in consequence of which the beer is very liable to become acid.

The wort is now transferred to the *fermenting tun*, where it is made to ferment by the addition of yeast, usually in the proportion of $\frac{1}{100}$th of its volume.

Yeast is a minute fungoid vegetable, which grows in solutions

containing sugar together with some nitrogenised substance (*e.g.*, a salt of ammonia), and the salts (phosphates of potash, soda, lime, and magnesia), which are essential constituents of its cells. It is only recently that the conditions under which the yeast plant grows have been ascertained, and the seeds or germs from which it originates have hitherto eluded detection, though it may be remarked that in this respect it only resembles some of the lower mosses, the vegetable character of which has never been called in question.

If a little white of egg, cheese, or a piece of flesh (all of which contain carbon, hydrogen, nitrogen, oxygen, and phosphates), be placed in a solution of sugar, and allowed to undergo decomposition, a grey scum forms upon the liquid, which is seen under the microscope to consist of irregularly oval cells, the growth of which may be watched under the microscope in a little of the liquid from which they were obtained, when they will be found to multiply rapidly by the production of new cells on all sides of them (fig. 289). The same cells will be developed very rapidly in the sweet wort of malt, allowed to undergo decomposition between 60° and 70° F.

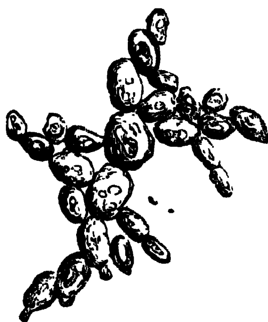
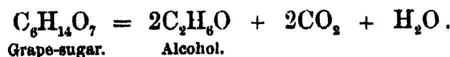


Fig 289.

These cells contain a substance somewhat resembling albumen, enclosed in a thin membrane, the composition of which is similar to that of cellulose. They also contain a peculiar nitrogenised body resembling diastase, and capable of inducing the conversion of cane-sugar ($C_{12}H_{22}O_{11}$) into grape-sugar ($C_6H_{14}O_7$). Accordingly, when yeast is added to a solution of cane-sugar, the liquid is found to increase in specific gravity (a solution of cane-sugar having a lower density than one containing an equivalent quantity of grape-sugar), previously to the commencement of fermentation, and the application of tests readily proves the presence of grape-sugar in the solution.

The grape-sugar then undergoes the decomposition known as *alcoholic fermentation*, which results in the production of alcohol, carbonic acid, lactic acid, succinic acid, glycerine, and a peculiar brown soluble matter, together with other substances, the true nature of which is yet undetermined. The fermentation is attended with a considerable elevation of temperature.

Taking into consideration only the alcohol and carbonic acid, which are the chief products, their formation from grape-sugar may be represented by the equation—



$$\underset{\text{Grape-sugar.}}{C_6H_{14}O_7} = \underset{\text{Alcohol.}}{2C_2H_6O} + 2CO_2 + H_2O.$$

During the fermentation the yeast cells are gradually broken up, so that a given quantity of yeast is capable of fermenting only a limited quantity of sugar. On an average, a quantity of yeast containing between two and three parts of solid matter is required to complete the fermentation of 100 parts of sugar. The solution remaining after the fermentation is found to contain salts of ammonia, which have been formed at the expense of the nitrogen of the yeast.

If the liquid in which the yeast excites fermentation contain nitro-

genised matters and phosphates, the yeast plant grows, and its quantity increases; thus in the sweet wort from malt, the yeast is nourished by the altered gluten and by the phosphates, so that it increases to six or eight times its original weight.

If yeast be heated to the boiling point of water, the plant is killed, as might be expected, and loses its power of inducing alcoholic fermentation; but it may be dried at a low temperature, or by pressure, without losing its fermenting power, and *dried yeast* is an article of commerce. German dried yeast is produced in the fermentation of rye for making Hollands.

Yeast will not cause fermentation in a solution containing more than one-fourth of its weight of sugar, and the fermentation is arrested when the alcohol amounts to one-fifth of the weight of the liquid, so that the strength of fermented liquors could never exceed 20 per cent. of alcohol. The fermentation is also arrested by the mineral acids, and by many of the substances to which antiseptic properties are commonly attributed, such as common salt, kreasote, corrosive sublimate, sulphurous acid, turpentine, &c.

In the fermentation of beer, the yeast is carried up to the surface by the effervescence due to the escape of the carbonic acid, and is eventually removed, in order to be employed for the fermentation of fresh quantities of wort.

When the fermentation has proceeded to the required extent, the beer is stored for consumption.

It will be seen that the chief constituents of beer are the alcohol, the nitrogenised substance derived from the albuminous matter of the barley, and not consumed in the growth of the yeast, the unaltered sugar and dextrine, the brown or yellow colouring matter formed during the fermentation, the essential oil and bitter principle of the hop.

Beer also contains acetic acid (formed by the oxidation of the alcohol, p. 487), free carbonic acid, which gives its sparkling character, together with the lactic and succinic acids and glycerine, formed as secondary products of the fermentation, and ammoniacal salts derived from the yeast. The soluble mineral substances from the barley are also present, *minus* the phosphates abstracted by the yeast.

The proportions of the constituents, of course, vary greatly, as will be seen from the following examples:—

Percentage of	Allsopp's Ale.	Bass's Ale.	Strong Ale.	Whitbread's Porter.	Whitbread's Stout.
Alcohol, ...	6·00	7·00	8·65	4·20	6·00
Acetic acid, ...	0·20	0·18	0·12	0·19	0·18
Sugar and other solid matters, . . .	5·00	4·80	6·60	5·40	6·38

The dark colour of porter and stout is caused by the addition of a quantity of *high-dried malt* which has been exposed to so high a temperature in the kiln as to convert a portion of its sugar into a dark brown soluble substance called caramel. It is said that alum and sulphate of iron are also added to porter and stout to cause them to froth strongly. The peculiar aroma of beer is probably due to the presence of a minute quantity of some fragrant ether, produced during the fermentation.

In some cases, when the operation of brewing has been badly con-

ducted, the beer becomes *ropy*, or undergoes the *viscous fermentation*. In this case the sugar suffers a peculiar transformation, resulting in the production of a mucilaginous substance resembling gum in its composition. This change may be induced in sugar by yeast which has been boiled, or by water in which flour or rice has been steeped. White wine occasionally becomes ropy from a similar cause, but red wines are not liable to this change, apparently because the tannin which they contain has precipitated in an insoluble form the ferment which induces it. During this viscous fermentation a part of the sugar is often converted into mannite ($C_6H_{14}O_6$).

351. ACETIFICATION—MANUFACTURE OF VINEGAR.—Beer which has become sour is often said to have undergone the *acetous fermentation;* but this is not strictly correct, the change being more similar to decay, since it is one in which the oxygen of the air directly takes part. The acidity of sour beer is caused by the acetic acid ($C_2H_4O_2$) formed by the action of atmospheric oxygen upon the alcohol, according to the equation—



$$C_2H_6O \text{ (Alcohol)} + O_2 = C_2H_4O_2 \text{ (Acetic Acid)} + H_2O.$$

Pure alcohol may be exposed to the air, either alone or when mixed with water, for any period, without suffering oxidation; but when in contact with certain changeable organic substances, the alcohol undergoes oxidation, and is converted into acetic acid. It is upon this circumstance that the different methods of producing vinegar are based.

The most direct application of this principle is made in the so-called *quick vinegar process* in use in continental countries where alcohol is free of duty. Alcohol of about 80 per cent. is mixed with 6 parts of water, and with about $\frac{1}{1000}$th part of yeast, or some other alterable substance containing nitrogen. This mixture is heated to about 80° F., and caused to trickle slowly from pieces of cord fixed in a perforated shelf over a quantity of wood shavings* previously soaked in vinegar, which is found materially to assist the acetification, and packed in a tall cask (fig. 290), in which holes have been drilled in order to allow the entrance of air. The oxidation of the alcohol soon raises the temperature to about 100° F., which occasions a free circulation of air among the shavings. The mixture is passed three or four times through the cask, and in about 36 hours the conversion into vinegar is completed. The oxidation of the alcohol in this process is found to be arrested by the presence of essential oils, or of kreasote, and similar antiseptic substances.

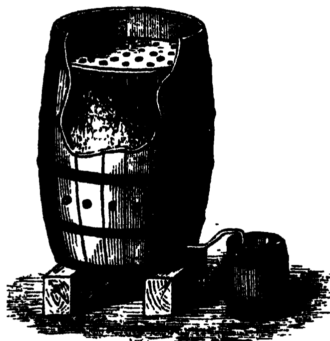
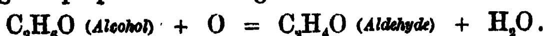


Fig. 290.

The necessity of affording a full supply of atmospheric air was not appreciated until Liebig had proved the existence of an intermediate stage in the process, consisting in a partial oxidation of the alcohol by which it became converted into *aldehyde* (C_2H_4O), an extremely volatile liquid

* These shavings appear to favour the process by serving as points of attachment for a microscopic vegetable, which encourages the oxidation of the alcohol.

(boiling at 70° F.), which was lost in the form of vapour, thus greatly diminishing the proportion of vinegar obtained—



$$C_2H_6O \text{ (Alcohol)} + O = C_2H_4O \text{ (Aldehyde)} + H_2O.$$

If a sufficient quantity of atmospheric air be supplied, the production of aldehyde is entirely avoided.

White wine vinegar is prepared in France from light wines by a process of much longer duration. A little boiling vinegar is poured into a cask, partially open at the top, together with four or five gallons of white wine which has been allowed to trickle over wood shavings. In a few days, during which the temperature is maintained at about 80° F., a fresh quantity of wine is poured in, and in the course of a fortnight half the vinegar contained in the cask is drawn off, and replaced by a fresh portion of wine. In this way an occasional renewal of the air in the upper part of the cask is provided for. The acetification is found to proceed more rapidly in old casks than in new ones, which is attributed to the presence of a peculiar conferva deposited upon the sides of the former, and styled *mother of vinegar*. It is probably for a similar reason that the acetification is promoted by the addition of ready-made vinegar at the commencement of the process.

In this country vinegar is chiefly prepared from malt, the infusion of which is allowed to undergo the alcoholic and acetous fermentation.

Vinegar contains on an average about 5 per cent. of acetic acid, together with small quantities of vegetable and mineral substances, varying with the source from which it was obtained. Its pleasant aroma is due to the presence of some *acetic ether* ($C_2H_5.C_2H_3O_2$) formed during its manufacture. The vinegar of commerce is allowed to be mixed with $\frac{1}{1000}$th of its weight of sulphuric acid in order to prevent it from becoming mouldy.

Bread.

352. The chemistry of fermentation is intimately connected with the ordinary process of bread-making. It will be remembered that wheaten flour (p. 479) consists, essentially, of starch and gluten, with a little dextrine and sugar. On mixing the flour with a little water, it yields a *dough*, the tenacity of which is due to the gluten present in the flour. If this dough be tied up in a piece of fine muslin, and kneaded under a stream of water, the starch will be suspended in the water, and will pass through the muslin, whilst the gluten will remain as a very tough elastic mass, which speedily putrefies if exposed to the air in a moist state, and dries up to a brittle horny mass at the temperature of boiling water.

On analysis, gluten is found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which may be represented by the empirical formula $C_{24}H_{40}N_6O_7$, though it cannot be regarded as a single independent substance, but as a mixture of three substances very closely allied in composition.

When gluten is boiled with alcohol, one portion refuses to dissolve, and has been named *vegetable fibrine*, from its resemblance to the substance forming the muscles of animals. When the solution in alcohol is allowed to cool, it deposits a white flocculent matter, very similar to the *caseine* which composes the curd of milk. On adding water to the cold alcoholic solution, a third substance (*glutine*) is separated, which much resembles the albumen found so abundantly in the blood.

The presence in gluten of three substances, similar to the three principal components of the animal body, leads us to form a high opinion of its value as a nutritive compound. But gluten itself, separated from the flour by the process above described, would be found very difficult of digestion, on account of its resistance to the solvent action of the fluids in the stomach ; indeed, the dough composed of flour and water is proverbially indigestible, even when baked. In order to render it fit for food, it must be rendered spongy or porous, so as to expose a larger surface to the action of the digestive fluids of the body; the most direct method of effecting this is the one adopted in the manufacture of the *aerated bread*, and consists in mixing the flour with water which has been highly charged, under pressure, with carbonic acid gas; the mixing having been effected in a strong closed iron vessel, an aperture in the lower part of this is opened, when the pressure of the accumulated gas forces the dough out into the air, and the gas which had been imprisoned in the dough expands, conferring great porosity and sponginess upon the mass in its attempt to escape. In another process for preparing *unfermented bread*, the flour is mixed with a little bi-carbonate of soda, and is then made into a dough with water acidulated with hydrochloric acid; the latter decomposing the bi-carbonate of soda, liberates its carbonic acid, which renders the bread porous. The chloride of sodium formed at the same time remains in the bread. In the preparation of cakes and pastry, the same object is sometimes attained by adding carbonate of ammonia to the dough; when heat is applied, in the baking, the salt is converted into vapour which distends the dough.

In the common process of bread-making, however, the carbonic acid destined to confer sponginess upon the dough is evolved by the fermentation of the sugar contained in the flour; the latter having been kneaded with the proper proportion (usually about half its weight) of water, a little yeast and salt are added, and the mixture is allowed to stand at a temperature of about 70° F. for some hours. The dough swells or *rises* considerably in consequence of the escape of carbonic acid, the sugar being decomposed into that gas and alcohol, as in ordinary fermentation. The spongy dough is then baked in an oven, heated to about 500° F., when a portion of the water and the whole of the alcohol are expelled, the carbonic acid being also much expanded by the heat, and the porosity of the bread increased. The granules of starch are much altered by the heat, and become far more digestible. Although the temperature of the inside of the loaf does not exceed 212° F. the outer portion becomes dry and hard, the hottest part being even torrefied or scorched into crust.

Occasionally, instead of yeast, *leaven* is employed, in order to ferment the sugar, leaven being dough which has been left in a warm place until decomposition has commenced.

The passage of new into stale bread does not depend, as was formerly supposed, upon the drying of the bread consequent upon its exposure to air, but is a true molecular transformation which takes place equally well in an air-tight vessel, and without any loss of weight. It is well known that when a thick slice of stale bread is toasted, which *dries* it still further, the crumb again becomes soft and spongy as in new bread; and if a stale loaf be again placed in the oven, it is entirely reconverted into new bread.

Wheaten flour is particularly well fitted for the preparation of bread on account of the great tenacity of its gluten. Next to wheat in this respect

stands rye, whilst the other cereals contain a gluten so deficient in tenacity that it is impossible to convert them into good bread.

Barley bread is close and heavy, since its nitrogenised matter is chiefly present in the form of albumen, which does not vesiculate like gluten, during the fermentation.

Even in wheaten flour the tenacity of the gluten is liable to variation, and in order to obtain good bread from a flour the gluten of which is inferior in this respect, it is customary to employ a minute proportion of alum. This addition being considered unwholesome by some persons, it would be better to substitute lime-water, which has been found by Liebig to have a similar effect. Sulphate of copper improves in a very striking manner the quality of the bread prepared from inferior flour, but this salt is far more objectionable than alum.

THE SUGARS.

353. The conversion of starch into grape-sugar, when heated in contact with diluted acids (p. 482), is taken advantage of for the preparation of this variety of sugar on the large scale. For this purpose, water acidulated with $\frac{1}{100}$th of sulphuric acid is heated to ebullition, and a hot mixture of starch and water allowed to flow gradually into it, so as not to reduce its temperature below the boiling point. The mixture is kept boiling for half-an-hour, after which chalk is added in small portions at a time to neutralise the sulphuric acid, and the sulphate of lime having been allowed to subside, the clear syrup is drawn off, and evaporated to the crystallising point. The conversion is accelerated by heating under pressure with steam at 320° F.

The grape-sugar or *glucose* thus manufactured cannot be employed as a substitute for the sugar extracted from the sugar-cane, on account of its greatly inferior sweetening power, which is less than half that possessed by cane-sugar.* It is, moreover, far less soluble in water, 1 part of grape-sugar requiring 1½ part of water to dissolve it, whilst cane-sugar requires only ⅓ part. Grape-sugar has been employed, however, for the adulteration of cane-sugar and honey. The fraud is easily detected in cane-sugar by boiling a portion of the sample with a little solution of potash, when the grape-sugar is decomposed, and colours the liquid intensely brown, pure cane-sugar giving very little brown colour unless boiled for a long time. A more delicate mode of detection consists in adding to a solution of the sugar a few drops of solution of sulphate of copper, and enough solution of potash to form an intensely blue liquid. The oxide of copper is not precipitated in the presence of either of the sugars; but if the blue liquid be very gently heated, a red precipitate of suboxide of copper will separate if grape-sugar be present, whilst with pure cane-sugar the precipitation does not take place unless the solution is boiled. Sulphate of lime will generally be detected in sugar or honey adulterated with glucose.

Even cellulose is transformed into dextrine and grape-sugar under the influence of sulphuric acid. If linen, calico, cotton-wool, or paper be dried, and gradually moistened with 1½ part of concentrated sulphuric acid, avoiding elevation of temperature, it is converted in the course of a few hours into a gummy mass which dissolves in water, and is very similar to dextrine. When the cellulose has been left in contact with

* Hence the loss of sugar by sweetening tarts before baking them, part of the sugar being converted into grape-sugar by the vegetable acids of the fruit.

the acid for a day or two, it should be dissolved in a large quantity of water, and boiled for 8 or 10 hours in order to effect the conversion into sugar; the acid may then be neutralised with chalk, the solution filtered from the sulphate of lime, and evaporated, when it furnishes a crystalline mass of grape-sugar.

Closely connected with the conversion of cellulose into dextrine by contact with strong sulphuric acid, is that very remarkable change of paper into *vegetable parchment*. If dry white blotting-paper be drawn through a cooled mixture of the strongest oil of vitriol with half its bulk of water, and be then thoroughly washed in a large volume of water, it becomes five times as strong as before, and has ⅘ths of the strength of ordinary animal parchment. The parchment paper, when dry, is found to have suffered no alteration in weight, and analysis shows its composition to be unchanged. This remarkable increase in strength must, therefore, be referred to a molecular alteration. The paper is also found to have become almost waterproof, and presents a somewhat translucent appearance like paper which has been slightly oiled. It receives many useful applications, for luggage labels which are not easily torn or removed by rain, and as a substitute for animal membrane in tying over preserves, &c.

This susceptibility of conversion into grape-sugar possessed by starch and cellulose, affords a very important clue in tracing the changes which take place in living vegetables. It has been already seen (p. 482) that during the germination of seeds, their starch is converted into sugar, in order that it may be carried in a soluble form to the extending limbs of the vegetable frame; but it would appear that in these parts, where a deposition of cellulose is required, the sugar ($C_6H_{14}O_7$) is reconverted into that substance ($C_6H_{10}O_5$). In the ripening of the fruit, however, the ligneous matter and the starch seem to be again converted into sugar, under the influence of the vegetable acids which unripe fruits contain.

Strictly speaking, the sugar contained in ripe fruits and in new honey is not grape-sugar ($C_6H_{14}O_7$), but a distinct variety of sugar known as *fruit sugar* or *fructose*, and having the composition ($C_6H_{12}O_6$). This sugar has also been designated, in reference to its characteristic feature, *uncrystallisable sugar*, and its production seems to constitute an intermediate stage in the transition of starch, cellulose, and cane-sugar into grape-sugar. Hence it is found that if the ebullition with diluted sulphuric acid be arrested as soon as the liquid becomes sweet, no crystals can be obtained, but on further ebullition, the fructose is converted into crystallisable glucose. When honey is kept for some time, the fructose gradually becomes converted into a crystalline mass of glucose. The same change is seen to take place in raisins, which contain granules of glucose, though the fresh grapes contain only fructose.

The uncrystallisable sugar forms the chief ingredient of *molasses* and *treacle*, for although the fresh juice of the sugar-cane contains no fructose, the treatment to which it is subjected in the extraction of the sugar occasions a copious formation of the uncrystallisable sugar at the expense of the cane-sugar. The simple ebullition of a solution of cane-sugar for a considerable period is said to convert a portion of it into fructose, and if a minute quantity of any uncombined acid be present, the change takes place very rapidly. Pure cane-sugar dissolved in water gradually changes into fructose when exposed to the light.

354. *Extraction of cane-sugar.*—In the extraction of sugar from the sugar-cane, the latter is cut before the period of flowering, when, as might be expected, this soluble nutriment of the plant is most abundant. For a similar reason, the canes are cut off close to the ground, since in the higher joints of the cane much of the sugar has already been consumed for their development.

A specimen of sugar-cane from Martinique was found to contain—

Juice, ...	90·1
Woody fibre, . .	9·9
	100·0

So that, theoretically, 100 parts of cane should yield as much as 90 parts of juice. The canes are crushed between iron cylinders, which express, under the best arrangements, only 65 parts of juice from 100 of cane. It has been found possible to increase the yield by steaming the canes before submitting them to a final pressure. The juice thus expressed contains about 18 per cent. of sugar, together with the usual components of the sap of plants, such as vegetable acids, albumen, salts, &c.

In the tropical climate in which the extraction is conducted, the albumen of the juice speedily alters when exposed to the air, and excites fermentation in the sugar, by which a considerable quantity would be lost. If the fresh juice were heated to coagulate the albumen, the free acid contained in it would change a portion of the sugar into the uncrystallisable variety. To avoid this, the juice is mixed with $\frac{1}{800}$th part of slaked lime, and is then heated to 140° F. in large flat copper pans. The coagulated albumen rises to the surface of the heavy syrup, and forms a thick scum, which is taken off, and the clear syrup is evaporated till it is strong enough to crystallise, when it is run off into shallow wooden vats, and allowed to cool for 24 hours. When briskly stirred, it congeals to a semi-solid mass of crystals, which are allowed to drain for three weeks in casks with perforated bottoms. The raw sugar thus obtained, after drying in the sun, is sent into commerce, the drainings being styled molasses or treacle. The weight of raw sugar seldom exceeds $\frac{1}{10}$th of the juice, that is, about half the quantity which the juice is known to contain, the remainder having been converted into uncrystallisable sugar during the process of extraction. The loss is found to be materially diminished by the use of *vacuum pans*, in which the evaporation of the syrup is conducted under diminished pressure, and therefore at a lower temperature. Greater economy is also introduced into the manufacture by the use of the crushed canes as fuel for the evaporating fires, and by restoring their ashes to the land as food for ensuing crops. The skimmings of the clarified juice are also advantageously used as manure.

The raw sugar obtained by the process just described contains about 60 per cent. of pure cane-sugar, the remainder consisting of water, uncrystallisable sugar, colouring matter, and various salts and other foreign substances derived from the cane-juice.

In the ordinary process of *sugar-refining*, two or three parts of raw sugar are dissolved in one part of water containing a little lime in solution, and mixed with three or four parts of ground bone-black for every hundred of sugar; a small quantity of serum of bullock's blood is also sometimes added. This mixture is heated by the passage of steam through it, when the albumen of the serum is coagulated, and rises to the surface

in the form of a scum which entangles the floating impurities as well as the bone-black, and leaves the syrup much lighter in colour, a considerable part of the colouring matter having been removed by the charcoal.

The syrup is then filtered through a thick layer of coarsely powdered bone-black, and is thus rendered perfectly colourless and ready for evaporation, which is conducted in a boiler with double sides, so that it may be heated by steam admitted between the two, and furnished with a dome from which the air may be exhausted in order to allow the evaporation to be conducted at a lower temperature, as well as out of contact with the atmospheric oxygen, so as to diminish as far as possible the production of uncrystallisable sugar. The boiling down of the syrup, which would require a temperature of 230° F. at the ordinary pressure, may thus be conducted at 160° F. When sufficiently evaporated,* the syrup is transferred to a heated vat, where it is stirred until a confused crystallisation commences, and is then drawn off into inverted sugar-loaf moulds of iron or earthenware, and allowed to crystallise during about 20 hours. The crystalline mass is then allowed to drain by the withdrawal of a plug at the apex of the inverted cone, and is washed with a little pure syrup to remove adhering colouring matter, after which the loaf is dried in an oven and finished by turning in a lathe.

The operation of washing with syrup is often referred to as *claying*, being sometimes effected by placing some powdered sugar upon the base of each loaf, and over this a cream of pure pipe-clay, the water draining from which dissolves the powdered sugar, and the syrup thus formed washes the loaf. The object of the clay appears to be simply to allow the water to flow gradually through the sugar.

The process of refining is sometimes shortened by washing the raw sugar with strong syrup, so as to remove the bulk of the impurities at the commencement, and a very ingenious method, known as the *centrifugal process*, has been devised for separating the syrup from the sugar thus washed. The pasty mixture of sugar and syrup is introduced into a cylinder of strong close metallic gauze, which is rapidly turned upon its axis, when the liquid syrup of course flies off through the apertures of the gauze, and is collected by a box surrounding the cylinder. A fresh quantity of syrup is then introduced, and separated in the same manner, so that the washing may be rapidly carried as far as may be deemed expedient.

355. During the wars of Napoleon, when the importation of sugar into France was suspended, this substance was extracted from the beet-root, and this process still forms a very important branch of French industry.

The white beet only is employed, on account of the difficulty of separating the colouring matter existing in the juice of the red variety. The juice contains about ten per cent. of cane-sugar, half of which only is usually obtained in the crystallised state. The process adopted for extracting it does not differ in principle from that applied to the juice of the sugar-cane.

Cane-sugar is also extracted in the United States from the sap of the sugar-maple, which is collected, usually in the spring, from deep incisions through the bark, into each of which a pipe of reed or elder is inserted

* The state of concentration of the syrup is known by the degree of viscidity which it exhibits between the finger and thumb, by the length of the thread to which it may be drawn, and by the mode in which this curls after breaking.

to conduct the juice into pans placed for its reception, whence it is removed before it has had time to become changed by fermentation. The juice is evaporated rapidly, and the raw crystalline mass sold without further refining. On an average, each tree furnishes about six pounds of sugar during the season.

Sugar-candy consists simply of large rhomboidal prismatic crystals of sugar deposited upon strings stretched across crystallising troughs, in which a strong syrup is slowly evaporated at about 170° F.

Barley-Sugar is prepared by evaporating the syrup beyond the crystallising point, till it solidifies, on cooling, to a vitreous mass, which is poured out on a cold surface and manipulated to the requisite forms. When kept for some time, the transparent barley-sugar becomes crystalline and opaque.

Caramel ($C_{12}H_{18}O_9$) is a dark brown substance produced by the action of a temperature of about 400° F. upon melted sugar. It is very soluble in water, and gives an intensely brown liquid, for which reason it is employed for colouring sauces, gravies, brandy, wines, &c.

356. *Chemical properties of the sugars.*—Although cane- and grape-sugar appear to be essentially indifferent substances, they are remarkably prone to form combinations with many basic metallic oxides. Thus a solution of cane-sugar is capable of dissolving a large quantity of lime, forming a compound ($CaO.C_{12}H_{22}O_{11}$) which is much more soluble in cold than in hot water, so that on boiling the transparent solution it becomes perfectly opaque, but resumes its transparency on cooling. This has been applied for separating the crystallisable sugar from molasses, the compound of sugar and lime precipitated by boiling being re-dissolved in cold water and treated with carbonic acid to separate the lime.

On boiling the hydrated oxide of lead with a solution of sugar, it is dissolved, and as the solution cools, a white powder is deposited, which has the composition $2PbO.C_{12}H_{18}O_9.H_2O$, the water being expelled at a temperature of 212°. The composition of this compound would lead to the belief that cane-sugar contains two molecules of constitutional water, and that its formula should be written $C_{12}H_{18}O_9.2H_2O$. By carefully heating cane-sugar, the compound, $C_{12}H_{20}O_{10}$, *saccharide*, has been obtained, and if this be further heated it yields $C_{12}H_{18}O_9$, *caramel*. When a solution containing 1 part of salt and 4 parts of sugar is allowed to evaporate spontaneously, it deposits a deliquescent compound containing $2(NaCl.C_{12}H_{18}O_9)\ 3H_2O$.

Many metallic oxides form compounds with sugar, which are readily soluble in alkaline liquids, so that the addition of sugar to solutions of the oxides of copper and iron, for example, prevents the precipitation of these oxides by the alkalies.

Grape-sugar also combines with many bases. The compounds which it forms with the alkalies are very unstable, and their solutions, which are at first alkaline, soon become neutral in consequence of the conversion of the grape-sugar into *glucic acid* ($H_8C_{12}H_{16}O_9$) by the loss of the elements of water.

By saturating a solution of grape-sugar with common salt, a liquid is obtained which deposits well-defined crystals, having the composition $2(C_6H_{12}O_6).NaCl.H_2O$. When dried at 212° it becomes $2(C_6H_{12}O_6).NaCl$. The true formula of grape-sugar is obviously $C_6H_{12}O_6.H_2O$, for if it be dissolved in hot strong alcohol (which dissolves far more grape-sugar than cane-sugar) it crystallises on cooling, in prisms, which have the formula $C_6H_{12}O_6$. A molecule of water may also be expelled from ordinary grape-sugar at 212° F.

The action of sulphuric acid upon cane- and grape-sugar is very different; the former is carbonised and completely decomposed, whilst the latter combines with the sulphuric acid to form *sulphosaccharic* acid, which yields soluble salts with lime and baryta.*

The optical properties of solutions of the sugars are now often turned to account for their identification, and even for the determination of their quantities. Grape-sugar and cane-sugar both rotate the plane of polarisation of a ray from left to right, cane-sugar having rather a more powerful action, but the uncrystallisable fruit-sugar

* *Ethyle-glucose*, a bitter, fragrant, oily substance, has been obtained by acting upon grape-sugar with bromide of ethyle and potash; it may be represented by the formula $C_6H_8(C_2H_5)_2O_6$.

rotates the plane in the opposite direction, from right to left. If a solution of cane-sugar, possessing the rotatory power from left to right, be heated with hydrochloric acid, it acquires the power of rotating the plane of polarisation from right to left, in consequence of the conversion into uncrystallisable sugar.

Starch-sugar exhibits three different modes of action upon polarised light, for a solution which has been kept some hours rotates the plane of polarisation only half as much as the freshly made solution; and if the sugar prepared from malt be dissolved in water, the solution has thrice the rotatory power which it possesses after being kept, and its rotatory power is one-third higher than that of the freshly dissolved starch-sugar. All these may be reduced at once to the lowest rotatory power by heating them nearly to ebullition and allowing them to cool.

357. *Mannite* ($C_6H_{14}O_6$), the sweet principle of manna (the concrete juice of the *Fraxinus ornus*), has already been noticed as one of the products of that peculiar kind of fermentation known as the *viscous*, to which beet-root juice is especially liable. It is also found in certain mushrooms, in sea weeds, celery, asparagus, and onions. By treating manna with hot alcohol, and allowing the filtered solution to cool, the mannite may be obtained in beautiful prismatic crystals, which have a sweet taste, and dissolve readily in water. Mannite differs widely from cane- and grape-sugar in not fermenting when placed in contact with yeast; and this circumstance, taken in conjunction with its composition, which differs so much from that of other members of the saccharine group, has always led to the belief that it was not properly classed among these.

Recent investigations have given it a place by the side of glycerine, the sweet principle of fats and oils, as will be seen hereafter.

Glycyrrhizine, the sweet principle of the liquorice root, somewhat resembles mannite, but does not crystallise.

GUN-COTTON AND SUBSTANCES ALLIED TO IT.

358. Starch, the sugars, and cellulose, when acted on by the strongest nitric acid, furnish compounds which are remarkable for their explosive character, and are formed by the substitution of nitric peroxide (NO_2) for a portion of the hydrogen. By far the most important of these is *pyroxyline* (πῦρ, *fire*, ξύλον, *wood*), which is produced by the action of nitric acid upon the different forms of woody fibre, including wood, cotton, and paper.

If a piece of white unsized paper (filter-paper) be soaked for a few minutes in the strongest nitric acid (sp. gr. 1·52), then washed in a large volume of water and allowed to dry, it will be found to have suffered little alteration in appearance or texture, but to have acquired the property of burning with almost explosive violence on the application of a flame or even of a moderately heated glass rod. This is due to the presence, in the altered paper, of a quantity of oxygen in the form of NO_2 (nitric peroxide), which serves to burn up the paper very rapidly, rendering it in great measure independent of any extraneous supply of oxygen. The NO_2 has been introduced into the paper in the place of an equivalent quantity of hydrogen, which has been converted into water by the third atom of oxygen in the nitric acid (HNO_3).

The pyroxyline so obtained, however, is always associated with a quantity of unaltered paper, for the water which is formed by the oxidation of the hydrogen, dilutes the remaining nitric acid, so that unless a very large proportion of nitric acid were employed, the acid would become so far weakened towards the close of the operation as to be incapable of converting the last portions of paper into pyroxyline. Moreover, since each fibre composing the paper is a very minute tube, often folded several times, it is not possible for the nitric acid to penetrate its entire substance unless the paper be soaked in it for a long time.

In order to effect a more complete conversion of the woody fibre into pyroxyline, the nitric acid must be mixed with strong sulphuric acid, which will combine with the water produced by the action of the nitric acid upon the hydrogen of the fibre, and will thus virtually maintain the nitric acid at its greatest strength throughout the operation. Cotton wool, from the looseness of its texture, is more easily converted into pyroxyline than paper.

The following proportions may be recommended for the preparation of gun-cotton on a small scale:—Dry 1000 grains of pure nitre (p. 424) at a very moderate heat, place it in a dry retort (fig. 291), pour upon it 10 drms. (by measure) of strong sulphuric acid, and distil until 6 drms. of nitric acid have passed over into the receiver. Dry some pure cotton wool, and weigh out 30 grains of it. Mix 2½ measured drachms of the nitric acid with an equal volume of strong sulphuric acid in a small beaker. Allow the mixture to cool, immerse the cotton wool, pressing it down with a glass rod, cover the beaker with a glass plate, and set it aside for fifteen minutes. Lift the cotton out with a glass rod, throw it into at least a pint of water, and wash it thoroughly in a stream of water till it no longer tastes acid or reddens blue litmus paper. Dry the cotton by exposure to air or at a very moderate heat.

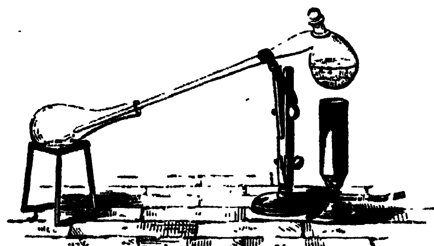


Fig. 291.

Very great attention has been paid to the manufacture of gun-cotton during the last few years, with the object of producing a perfectly uniform product which might be employed as a substitute for gunpowder.

The following is an outline of the process now generally adopted for the production of large quantities of gun-cotton by Abel's process:—

359. *Manufacture of gun-cotton.*—The cotton is employed in the form of the waste cuttings from spinning machines (cotton waste).

The proportions in which it is found most advantageous to mix the nitric and sulphuric acids are 1 part of nitric acid (sp. gr. 1·52) and 3 parts by weight (or 2·45 by volume), of sulphuric acid (sp. gr. 1·84). These proportions of the acids are placed in separate stoneware cisterns with taps, and allowed to run simultaneously, in slow streams, into another stoneware cistern furnished with a tap and an iron lid, through a second opening in which an iron stirrer is employed to mix the acids thoroughly. The mixture is set aside for several hours to become perfectly cool.

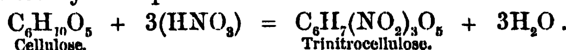
A quantity of the mixed acids is drawn off into a deep stoneware pan standing in cold water, and provided with a perforated iron shelf, upon which the cotton may be drained. The well-dried cotton is immersed, a little at a time, in the acid, and stirred about in it for two or three minutes with an iron stirrer. It is then placed upon the perforated shelf, and the excess of acid squeezed out with the stirrer. Enough acid is drawn from the cistern to replace that which has been absorbed by the cotton, and more cotton is treated in the same way. Since a considerable rise of temperature is produced by the action of the nitric acid upon the cotton, it is necessary to keep the pan surrounded with cold water. A large proportion of the cotton is doubtless converted into gun-cotton in this preliminary immersion in the mixed acids; but in order to convert the remainder, it is necessary to allow the cotton to remain in contact with the acid for a much longer period, so as to ensure its penetration into every part of the minute twisted tubes of the fibre. The preliminary immersion of each skein has the advantage of wetting every part with the acid, which could not be so certainly effected if several skeins were thrown at once into a jar, and of preventing the great accumulation of heat which would ensue if the entire chemical action were allowed to take place upon a number of skeins at the same time. The amount of heat evolved during the subsequent soaking in acid is comparatively small.

The skeins are next transferred to a jar with a well-fitting cover, in which they

are pressed down and completely covered with the mixed acids, of which from 10 to 15 times the weight of the cotton will be required, according to the closeness with which the skeins are packed in the jar. The jar is placed in cold water, and the cotton allowed to remain in the acid for 24 hours.

The skeins are then removed, with the aid of an iron hook, to a centrifugal extractor, which is a cylinder made of iron or copper gauze, through which the liquid is whirled out by the rapid rotation of the cylinder upon an axle. In this they are whirled, at first slowly, and afterwards at 800 revolutions per minute, during ten minutes, when the bulk of the acid is separated. In order to wash away the remainder of the acid, the cotton is plunged, suddenly, in very small portions, into a large volume of water; for if the water were allowed to come slowly into contact with the mixed acids, so much heat would be evolved as to decompose a portion of the pyroxyline. The cotton is then drained in the centrifugal extractor, and again rinsed in much water. After two or three rinsings it is reduced to pulp in a rag-engine such as is employed in paper-mills. The pulp is thoroughly washed by being well stirred up by a *poaching-engine* for about 48 hours in a stream of warm water, so as to remove every trace of acid, which is assisted by rendering the water alkaline with a little lime or carbonate of soda. The pulp is then drained, moulded into discs or any other required form, condensed by hydraulic pressure until it has about the same specific gravity as water, and dried upon heated plates. As it leaves the hydraulic press, the cotton contains about one-fifth of its weight of water, so that it may, if required, be cut up or bored without danger of explosion.

360. *Chemical composition of gun-cotton.*—Perfectly pure gun-cotton contains carbon, hydrogen, nitrogen, and oxygen, in proportions which correspond to the empirical formula $C_6H_7N_3O_{11}$. The determination of its rational formula is attended with difficulty, because, being an indifferent substance, it does not form definite combinations with other bodies of known molecular weight, and it is, of course, impossible to arrive at its volume in the state of vapour, which so frequently affords valuable assistance in fixing a rational formula. Having regard to the mode of its formation from cellulose (cotton), $C_6H_{10}O_5$, by the action of nitric acid, without evolution of gas, the most probable rational formula appears to be $C_6H_7(NO_2)_3O_5$, which represents it as *trinitrocellulose*, or cellulose in which three molecules of nitric peroxide have been substituted for three atoms of hydrogen. The action of nitric acid upon the cotton would then be represented by the equation—

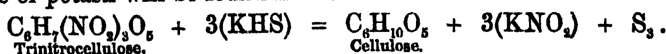


$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + 3(HNO_3) = \underset{\text{Trinitrocellulose.}}{C_6H_7(NO_2)_3O_5} + 3H_2O.$$

According to this equation, 100 lbs. of cotton should furnish 183 lbs. of gun-cotton; but in practice only about 177 lbs. are obtained, a part of the deficiency being accounted for by unavoidable mechanical loss, and by small quantities of foreign matters dissolved out by the acids.

That the nitrogen is really present in the gun-cotton in the form of nitric peroxide (NO_2), as implied in the above formula, is indicated by the action of potash, which dissolves the gun-cotton, and yields a solution containing nitrate and nitrite of potash, exactly the products which are formed by the action of potash upon nitric peroxide (p. 141).

Another reaction of gun-cotton which supports the above view of its constitution, is that with hydrosulphate of potassium. If some hydrate of potash be dissolved in alcohol, and the solution saturated with gaseous hydrosulphuric acid, an alcoholic solution of hydrosulphate of potassium (KHS) is obtained; and if the gun-cotton be immersed in this solution, and gently heated, it will be rapidly reconverted into ordinary cotton, and nitrite of potash will be found in the solution—



$$\underset{\text{Trinitrocellulose.}}{C_6H_7(NO_2)_3O_5} + 3(KHS) = \underset{\text{Cellulose.}}{C_6H_{10}O_5} + 3(KNO_2) + S_3.$$

This is the so-called synthetical method of determining the composition

of gun-cotton, for of course 183 parts of the latter should furnish 100 parts of cotton.

361. *Products of the explosion of gun-cotton.*—From what has been stated with respect to the products of explosion of gunpowder (p. 423), it might be expected that those furnished by gun-cotton would vary according to the conditions under which the explosion takes place. When a mass of the gun-cotton wool is exploded in an unconfined state, the explosion is comparatively slow (though appearing to the eye almost instantaneous), since each particle is fired by the flame of that immediately adjoining it, the heated gas (or flame) escaping outwards, so that some time elapses before the interior of the mass is ignited. But when the gun-cotton is enclosed in a strong case, so that the flame from the portion first ignited is unable to escape outwards, and must spread into the interior of the mass, this is ignited simultaneously at a great number of points, and the decomposition takes place far more rapidly; a given weight of cotton being thus consumed in a much shorter time, a far higher temperature is produced, and the ultimate results of the explosion are much less complex, as would be expected from the well-known simplifying effect of high temperatures upon chemical compounds.

If a tuft of gun-cotton wool be placed at the bottom of a tall glass cylinder, and inflamed by a heated wire, it will be seen that, immediately after the explosion, the gas within the cylinder is colourless, but it soon becomes red, showing that nitric oxide was present among the products, and became converted into nitrous acid and nitric peroxide by the oxygen of the air. Of course these are strongly acid, and hence the acid character of the moisture deposited in the barrel of a fowling-piece in which gun-cotton cartridges are employed. In order to avoid corrosion of the barrel it is necessary that it should be cleaned at the end of the day's shooting.

A little hydrocyanic acid can be detected among the products of combustion of loose gun-cotton.

The determination of the products of explosion of confined gun-cotton has been effected by Karolyi in the same manner as in the case of gunpowder (see p. 418), by enclosing the cotton in a cast-iron cylinder, strong enough to resist bursting until the combustion of the last portion of the charge, which was suspended in an iron globe exhausted of air, and exploded by the galvanic battery; the total volume of the gases collected in the globe was then determined and subjected to analysis. The amount of gun-cotton fired was about 150 grains. Unfortunately, the formula given for the sample of gun-cotton experimented on does not represent the trinitrocellulose which constitutes pure gun-cotton, being $C_{12}H_{17}N_5O_{19}$, instead of $C_{12}H_{14}N_6O_{22}$ (representing 2 molecules of trinitrocellulose), but the difficulty attending the exact ultimate analysis of gun-cotton is so great, that there is greater probability of the analysis being incorrect than of the composition of the cotton having really differed materially from that of trinitrocellulose. 100 grains of gun-cotton gave a quantity of aqueous vapour and gaseous products, calculated to occupy, at 60°·8 F. and 29·06 in. Bar., 325·5 cubic inches, supposing the aqueous vapour to remain uncondensed at that temperature. The analysis of the gas proved that 100 volumes of the products of explosion contain—

Aqueous vapour, . .	25·34 vols.
Carbonic oxide (CO), .	28·95 ,,
Carbonic acid (CO_2) . .	20·82 ,,
Nitrogen, ...	12·67 ,,
Hydrogen, ...	3·16 ,,
Marsh-gas (CH_4), . .	7·24 ,,
	98·18 ,,

If the marsh-gas and hydrogen be left out of consideration, the following equation will account for the other products of the explosion, supposing the gun-cotton to be pure trinitrocellulose—



$$2C_6H_7(NO_2)_3O_5 = 9CO + 3CO_2 + 7H_2O + N_6.$$

According to this equation, 100 grains of gun-cotton should furnish 356 cubic inches of gas and vapour, instead of 325·5 as determined by experiment, and the volumes of the products should be—

Aqueous vapour, . . .	28 vols.
Carbonic oxide, . . .	36 ,,
Carbonic acid, . . .	12 ,,
Nitrogen, ...	12 ,,

which do not agree with the experimental results. It is not to be expected, however, that one simple equation should correctly represent all the products of such a decomposition (see p. 420).

A cubic inch of compressed gun-cotton, of the same density as water, weighs about 250 grains, and would evolve, according to the above equation, 865 cubic inches of gas and vapour at 60° F., supposing the steam to be capable of remaining uncondensed.

A cubic inch of gunpowder, of density 1·75, weighs about 440 grs., and would evolve by calculation (p. 420) about 390 cub. in. of gas at 60° F. This would become 4156 cubic inches at the calculated temperature of the explosion, corresponding to a pressure of about 26 tons per square inch. The quantity of heat generated in the explosion of gun-cotton has not been determined, but if it be identical with that evolved by gunpowder, the temperature of the flame of gun-cotton would be 2166° C. (= 3930° F.), a temperature much lower than in the case of gunpowder, because the specific heats of the products from gun-cotton are higher. At that temperature, the 865 cubic inches of gas generated by a cubic inch of gun-cotton would become about 7720 cubic inches, and would exert a pressure of about 50 tons upon the square inch, or nearly twice that calculated for gunpowder.

The experiments hitherto made have been unfavourable to the employment of gun-cotton as a substitute for gunpowder in artillery, on account of the injury which its violent explosion occasionally inflicts upon the gun. For use in fowling-pieces, the gun-cotton pulp is diluted with a proportion of ordinary cotton pulp, and made into a kind of paper which is rolled up to form the cartridges. Although such cartridges leave a considerable carbonaceous residue when fired on a plate, they leave little or no residue when fired under pressure.

If a piece of compressed gun-cotton be kindled with a hot wire it burns rapidly away, producing a large volume of flame, but without any explosive effect.* In order that gun-cotton fired in this manner might be used for destructive purposes, it was found necessary to confine it in strong cases, so that the flame of the portion first ignited should be employed in raising the temperature of the rest to the exploding point.

The discovery, made by E. O. Brown, of a method by which the *unconfined* gun-cotton could be made to explode with most destructive violence,

* Too much stress, however, should not be laid upon this as rendering gun-cotton magazines safer in case of fire than gunpowder magazines. The experiment with gunpowder mentioned at page 423, shows that if all the particles of an explosive be raised at once to nearly the inflaming point, the first particle which inflames will cause the detonation of the remainder. Since the inflaming point of gun-cotton is low, the above condition would be easily fulfilled in a conflagration.

has opened a new career to this material, rendering it far superior to gunpowder for all blasting operations, torpedoes, &c. It is only necessary to explode in contact with the compressed cotton a *detonating fuze*, consisting of a little tube of quill or thin metal charged with a few grains of fulminate of mercury, to cause the cotton to detonate with extreme violence; and such detonation can be communicated along a row of pieces of compressed cotton placed at short distances from each other.

This capability of undergoing what may be termed *sympathetic explosion* is by no means confined to gun-cotton. Previously to Brown's discovery, Nobel had shown it to exist in the case of nitroglycerine, and Abel afterwards proved that most explosives, including even gunpowder, can be made to detonate in a similar manner. The *modus operandi* of the detonating fuze has not, however, been satisfactorily explained. It would at first appear to act merely by mechanical concussion, but the results obtained by Abel throw some doubt upon this.

The very destructive effect of the gun-cotton exploded in this way is, of course, due to the sudden manner in which the whole mass is resolved into gaseous products.

362. *Properties of gun-cotton compared with those of gunpowder.*—Gun-cotton is more easily exploded than gunpowder; the latter requires a temperature of at least 600° F., whilst gun-cotton may explode at 277° F., and must explode at 400° F. It is very difficult to explode gunpowder by percussion, even between a steel hammer and anvil; but gun-cotton invariably detonates in this way, though the explosion is confined to the part under the hammer. The explosion of gun-cotton is, of course, unattended by any smoke, a most important advantage in mines, the atmosphere of which is sometimes rendered almost intolerable by the smoke of gunpowder used in blasting. The absence of residue from the gun-cotton prevents the fouling of guns, and renders it unnecessary to sponge them after each discharge, for the amount of incombustible mineral matter present in the cotton is very small (from 1 to 2 per cent.), and is entirely scattered by the explosion.

It has already been mentioned that the explosion of gun-cotton does not impart so much heat to the metal of the gun as that of powder, the difference being so great that, after firing 100 rounds with gun-cotton, the gun was not so much heated as after 30 rounds with gunpowder. This important advantage of gun-cotton may be due either to the lower temperature of its flame, or to the circumstance that the charge of gun-cotton is only one-third of the charge of powder, that the explosion of the former is so much more rapid, leaving less time for the communication of heat to the metal, and that there are no highly-heated solid products left in contact with the gun. Gun-cotton wool may be fired upon the palm of the hand with impunity, or upon a heap of gunpowder without kindling it; although it cannot be doubted that the temperature of the flame is really much higher than the inflaming point of powder. That the recoil of a gun charged with gun-cotton is only two-thirds of that experienced with gunpowder, is probably due to the rapidity of the explosion, which allows less time for overcoming the inertia of the gun; the difference in recoil taking the form of strain upon the metal composing the gun.

It is evident, from the consideration of its manufacture, that gun-cotton is entirely uninjured by water, so that a store of this explosive might be immersed in water in case of need, and would be still serviceable after

drying, whereas gunpowder is, of course, rendered useless by contact with water, which dissolves out the nitre. Even when exposed to very damp air, gunpowder is liable to injury from the effect of moisture in partially separating the nitre from the other ingredients, whilst gun-cotton only requires exposure to a dry atmosphere for a short time to render it fit for use. The proportion of moisture retained by gun-cotton, in the ordinary state of the atmosphere, is 2 per cent.

As an objection to the employment of gun-cotton as a substitute for gunpowder, it has been asserted that the trinitrocellulose is liable to undergo spontaneous decomposition, which might at any time render the contents of a magazine unserviceable, or might even give rise to the evolution of a sufficient amount of heat to cause an explosion. The origin of this objection is to be traced to the old process for preparing gun-cotton, in which the acids were not allowed to act upon the cotton for a sufficient length of time, so that the whole of the cotton was not converted into true gun-cotton, but some less stable substitution products were formed at the same time. Another cause of spontaneous alteration is the imperfect washing of the gun-cotton, whereby minute traces of acid are left in the fibre. All recent experiments, by Abel and others, appear to have proved that, considering its highly complex character, *pure* gun-cotton is a very stable compound under ordinary conditions; although, when kept in a moist state, it developes traces of acid products, the temperature does not rise to any important extent, nor is the explosive quality of the material at all injured.

363. Gun-cotton is somewhat harsher to the touch than ordinary cotton, and becomes remarkably electrical when rubbed between the dry fingers. It is insoluble in alcohol and ether, as well as in a mixture of these solvents, though ordinary specimens generally yield a small percentage of soluble matter when treated with a mixture of alcohol and ether, because they contain extraneous matters, such as the other substitution products to be mentioned presently. Acetic ether dissolves it, and so does a mixture of ordinary ether with ammonia. Strong sulphuric acid dissolves it without carbonisation, unless any unconverted cotton should happen to be present.

364. *Collodion cotton.*—When cotton or paper is acted upon by a mixture of nitric and sulphuric acids containing more water than is present in that employed for the preparation of gun-cotton (p. 496), compounds are formed which contain less nitric peroxide, and are much less combustible than the trinitrocellulose, from which they are also distinguished by their solubility in mixtures of alcohol and ether.

In order to render evident the relations between these compounds and gun-cotton, the formula of the latter must be trebled, when we have the following series of nitro-compounds produced by the mixtures of nitric acid, sulphuric acid, and water, to which they stand opposite—

Composition of the mixed acids.	Products of their action on cellulose.
(1.) $HNO_3 + H_2O.SO_3$	$C_{18}H_{21}(NO_2)_9O_{15}$
(2.) $HNO_3 + H_2O.SO_3 + 1\frac{3}{4}H_2O$	$C_{18}H_{22}(NO_2)_8O_{15}$
(3.) $HNO_3 + H_2O.SO_3 + 2H_2O$	$C_{18}H_{23}(NO_2)_7O_{15}$
(4.) $HNO_3 + H_2O.SO_3 + 2\frac{1}{2}H_2O$	$C_{18}H_{24}(NO_2)_6O_{15}$

As might be expected, these compounds diminish in combustibility in proportion as the NO_2 contained in them diminishes. The second is that

employed for the preparation of photographic collodion, being dissolved for that purpose in a mixture of ether and alcohol.

In order to prepare the soluble cotton for collodion, three measured ounces of ordinary nitric acid (sp. gr. 1·429) are mixed with two ounces of water in a pint beaker. Nine measured ounces of strong sulphuric acid (sp. gr. 1·839) are added to this mixture, which is continually stirred whilst the acid is being added. A thermometer is placed in the mixture, which is allowed to cool to 140° F.; 100 grains of dry cotton wool, in ten separate tufts, are immersed in the mixture for five minutes, the beaker being covered with a glass plate. The acid is then poured into another beaker, the cotton squeezed with a glass rod, and thrown into a large volume of water; it is finally washed in a stream of water till it is no longer acid, and dried by exposure to air. (By adding to the acid which was drained out of the cotton, three drachms more sulphuric acid, and immersing another 100 grains of cotton for *ten* minutes, a second portion of soluble cotton may be obtained.)

Collodion balloons.—These balloons may be made in the following manner:—6 grains of the collodion cotton, prepared according to the above directions, are dissolved in a mixture of 1 drachm of alcohol (sp. gr. ·835) and 2 drachms of ether (sp. gr. ·725), in a corked test-tube. The solution is poured into a dry Florence flask, which is then turned about slowly, so that every part of its surface may be covered with the collodion, the excess of which is then allowed to drain back into the tube. Air is then blown into the flask through a long glass tube attached to the bellows (or to the blowpipe-table (fig. 131), as long as any smell of ether is perceptible. A pen-knife blade is carefully inserted between the flask and the neck of the balloon, which is thus detached from the glass all round; a small piece of glass tubing is introduced for an inch or two into the neck of the balloon, so that the latter may cling round it. Through this tube air is drawn out by the mouth until one-half of the balloon has left the side of the flask and collapsed upon the other half; by carefully twisting the tube, the whole of the balloon may be detached and drawn out through the neck of the flask, when it must be quickly untwisted, distended by blowing through the tube, tied with a piece of silk, and suspended in the air to dry. The average weight of such balloons is two grains.

When collodion-cotton is kept for some time, especially if at all damp, it undergoes decomposition, filling the bottle with red fumes, and becoming converted into a gummy mass, which contains oxalic acid.

365. *Xyloidine* is the name given to a highly combustible substance analogous to pyroxyline, which is obtained by dissolving starch in the strongest nitric acid, and diluting the solution with water, when the xyloidine falls as a white precipitate, which may be collected upon a filter, and washed till free from acid. The composition of xyloidine is $C_6H_8(NO_2)_2O_5$, representing starch ($C_6H_{10}O_5$), in which 2 molecules of nitric peroxide have been substituted for 2 atoms of hydrogen.

Nitromannite ($C_6H_8(NO_2)_6O_6$) is another explosive body of the same order, obtained by adding powdered mannite ($C_6H_{14}O_6$), in small portions, to a mixture of equal measures of the strongest nitric and sulphuric acids, which immediately dissolve it, and presently solidify to a mass of minute needles of nitromannite, which may be washed with a large volume of water, and crystallised from boiling alcohol. Under the hammer, nitromannite explodes with a very loud report. When heated, it fuses before exploding.

WINE AND SPIRITS.

366. Wine is essentially composed of 8 or 10 parts of alcohol, with 85 or 90 of water, together with minute quantities of certain fragrant ethers, of colouring matter, of bitartrate of potash, and of the mineral substances derived from the grape-juice. Glycerine and succinic acid have also been found in wines, and appear to be constant secondary products of the alcoholic fermentation (p. 485).

Those wines in which the whole of the sugar has been fermented are known as *dry* wines; whilst *fruity* wines still retain a considerable quantity of sugar.

The preparation of wine differs from that of beer in the circumstance that no addition of ferment is necessary, the fermentation being excited by a substance present in the grape-juice. This juice contains, in addition to grape-sugar, vegetable albumen, tartrate of potash, and the usual mineral salts found in vegetable juices. The husks, seeds, and stalks of the grape contain a considerable quantity of tannin, together with certain blue, red, and yellow colouring matters.

When the expressed juice remains for a short time in contact with the air, the albuminous substances contained in it enter upon a state of change, exciting the vinous fermentation in the sugar, and a scum of yeast is formed upon the surface. If this fermentation takes place in contact with the husks of the dark grapes, the alcohol dissolves the colouring matter, and a red wine results; whilst for the production of white wines, the husks, &c., are separated previously to the fermentation, and the juice is exposed as little as possible to the air.

White wines are rather liable to become *ropy* from viscous fermentation, but this is prevented by the addition of a small quantity of tannin, which precipitates the peculiar ferment. The tannin for this purpose is extracted from the husks and stalks of the grapes themselves.

Red wines, such as port and claret, are often very astringent from the tannin dissolved out of the husks, &c., during the fermentation. Port wine, when freshly bottled, still retains in solution a considerable quantity of bitartrate of potash ($KHC_4H_4O_6$), but after it has been kept some time, and become more strongly alcoholic, this salt is deposited, together with a quantity of the colouring matter, in the form of a crust upon the side of the bottle. Thus a dark *fruity* port becomes *tawny* and *dry* when kept for a sufficient length of time, the sugar having been converted into alcohol.

When the wine contains an excess of tartaric acid, it is customary to add to it some neutral tartrate of potash ($K_2C_4H_4O_6$), which precipitates the acid in the form of bitartrate.

The preparation of champagne is conducted with the greatest care. The juice or *must* is carefully separated from the *marc* or husk, and is often mixed with one per cent. of brandy before fermentation. After about two months the wine is drawn off into another cask, and clarified with isinglass dissolved in white wine, and added in the proportion of about half-an-ounce to 40 gallons. This combines with the tannin to form an insoluble precipitate, which carries with it any impurities floating in the wine. After another interval of two months, the wine is again drawn off, and a second clarification takes place; and in two months more the wine is drawn off into bottles containing a small quantity of pure sugar-candy dissolved in white wine. The bottles, having been securely corked and wired, are laid down upon their sides for eight or ten months,

during which time the fermentation of the newly added sugar takes place, and the carbonic acid produced dissolves in the wine, whilst a quantity of yeast is separated. In order to render the wine perfectly clear, the bottle is left for about three weeks in such a position that the deposit may subside into the neck, against the cork, which is then unwired so that the pressure of the accumulated carbonic acid may force it out together with the deposit; the bottle having been rapidly filled up with white wine, is again corked, wired, covered with tin foil, and sent into the market. Pink champagne is prepared from the must which is squeezed out of the marc after it has ceased to run freely, and contains a little of the colouring matter of the husk. The colour is also sometimes imparted by adding a little tincture of litmus.

The proportion of alcohol in wines varies greatly, as will be seen from the following statement of the weight of alcohol in 100 parts of the wine :—

Port, ...	from 15 to 17.
Sherry, . . .	„ 14 to 16.
Champagne, . .	11·5.
Claret, . . .	„ 8 to 9.
Rudesheimer, .	„ 7 to 8·5.

Sherry contains from 1 to 5 per cent. of sugar, port from 3 to 7 per cent., and Tokay 17 per cent.; in the last case, the sugar is increased by adding some of the must concentrated by evaporation to the wine previously to bottling.

The *bouquet* or fragrance of wine is due to the presence of certain fragrant ethers, especially of œnanthic, pelargonic, and acetic ether, formed during the fermentation or during the subsequent storing of the wine. It is to the increased quantity of such fragrant ether that the superior bouquet of many old wines is due.

367. *Distilled spirits.*—The varieties of ardent spirits are obtained from fermented liquids by distillation, so that they consist essentially of alcohol more or less diluted with water, and flavoured either with some of the volatile products of the fermentation, or with some essential oil added for the purpose.

Brandy is distilled from wine, and coloured to the required extent with burnt sugar (caramel). Its flavour is due chiefly to the presence of œnanthic ether derived from the wine. The colour of genuine pale brandy is due to its having remained so long in the cask as to have dissolved a portion of brown colouring matter from the wood, and is therefore an indication of its age. Hence arose the custom of adding caramel, and sometimes infusion of tea, to impart the astringency due to the tannin dissolved from the wood by old brandy.

Whisky is distilled from fermented malt, which has been dried over a peat fire, to which the characteristic smoky flavour is due.

Gin is also prepared from fermented malt or other grain, and is flavoured with the essential oil of juniper, derived from juniper berries, added during the distillation.

Rum is distilled from fermented molasses, and appears to owe its flavour to the presence of butyric ether, or of some similar compound.

Arrack is the spirit obtained from fermented rice.

Kirschwasser and *maraschino* are distilled from cherries and their stones, which have been crushed and fermented.

Some varieties of British brandy and whisky are distilled from fer-

mented potatoes, or from a mixture of potatoes and grain, when there distils over, together with ordinary alcohol, another spirit belonging to the same class, but distinguished from alcohol by its nauseous and irritating odour. This substance, which is known as *potato-spirit*, *amylic alcohol*, or *fousel oil* ($C_5H_{12}O$) also occurs, though in very minute quantity, in genuine wine-brandy. The manufacturers of spirit from grain and potatoes remove a considerable part of this disagreeable and unwholesome substance by leaving the spirit for some time in contact with wood-charcoal.

THE ALCOHOLS AND THEIR DERIVATIVES.

368. It has already been stated that alcohol is the type of a very important class of compounds closely related to each other in composition and properties.

The alcohols are all composed of carbon, hydrogen, and oxygen; the members of the series represented by common alcohol always contain one atom of oxygen. The number of atoms of hydrogen is always an even number, exceeding by *two* the doubled number of atoms of carbon, so that the *general formula of an alcohol of this series* may be written thus, $C_nH_{2n+2}O$. Thus, in ordinary or *vinic* alcohol, C_2H_6O, $n = 2$, in wood-spirit or *methylic* alcohol, CH_4O, $n = 1$, in potato-spirit or *amylic* alcohol, $C_5H_{12}O$, $n = 5$.

These alcohols constitute, therefore, a truly homologous series (p. 454) of which many members, however, remain to be discovered.

The following table includes the alcohols of this series which are at present known :—

Chemical Name.	Source.	Formula	Common Name.
1. Methylic alcohol	Destructive distillation of wood	$C\ H_4\ O$	Wood naphtha
2. Ethylic ,,	Vinous fermentation of sugar	$C_2\ H_6\ O$	Spirit of wine
3. Propylic ,,	Fermentation of grape-husks	$C_3\ H_8\ O$	
4. Butylic ,,	Fermentation of beet-root .	$C_4\ H_{10}O$	
5. Amylic ,,	Fermentation of potatoes .	$C_5\ H_{12}O$	Fousel oil
6. Caproic ,,	Fermentation of grape-husks	$C_6\ H_{14}O$	
7. Œnanthic ,,	Distillation of castor-oil with potash	$C_7\ H_{16}O$	
8. Caprylic ,,	Fermentation of grape-husks	$C_8\ H_{18}O$	
10. Rutic ,,	Oil of rue	$C_{10}H_{22}O$	
12. Lauric ,,	Whale oil	$C_{12}H_{26}O$	
16. Cetylic• ,,	Spermaceti	$C_{16}H_{34}O$	Ethal
27. Cerylic ,,	Chinese wax	$C_{27}H_{56}O$	Cerotene
30. Melissic ,,	Bees' wax	$C_{30}H_{62}O$	Melissine

The usual gradation in properties attending the gradation in composition among the members of a homologous series, is strikingly exemplified in the class of alcohols. The first eight members of the group, linked together as they are by an almost common origin (being derived, with one exception, from the fermentation of substances nearly allied, and that exception being a product of destructive distillation which may be regarded as an accelerated fermentation), and by a regularly ascending com-

position, would be expected to resemble each other in their properties far more closely than the other members of the class. Accordingly, we find that methylic, ethylic, propylic, butylic, amylic, caproic, œnanthic,* and caprylic alcohols, are all liquid at the ordinary temperature, that they all possess peculiar and powerful odours, and may be readily distilled unchanged. Among these, however, the gradation is not to be overlooked. The two first, methylic and ethylic alcohols, may be mixed with water in all proportions, but the third, propylic alcohol, though freely soluble in water, is not so to an unlimited extent; whilst butylic alcohol is less soluble, and amylic alcohol may be said to be sparingly soluble in water. Caproic alcohol, the next member, is insoluble in water; whilst caprylic is not only insoluble, but possesses an oily character, leaving a greasy stain upon paper.

In their boiling points, and the specific gravities of their vapours, a similar gradation is observed.

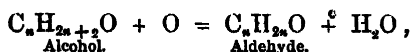
Alcohol.	Boiling Point.	Vapour Density.
Methylic, ...	149°·9 F.	1·12
Ethylic, ...	173°	1·61
Propylic, ...	205°	2·02
Butylic, ...	233°	2·59
Amylic, ...	269°·8	3·15
Caproic, ...	299°-309°	3·53
Œnanthic, ...	327°-343°	—
Caprylic, ...	356°	4·50

One molecule of each of these alcohols yields *two volumes* of vapour; or, in other words, if a given weight of the alcohol corresponding to its molecular weight be converted into vapour, that vapour will occupy twice as much space as would be occupied by one part of hydrogen at the same temperature and pressure.

The higher members of the group of alcohols are solid fusible bodies more nearly approaching to waxy or fatty matters in their nature, and not susceptible of distillation without decomposition. Far less is known of these than of the alcohols containing less carbon.

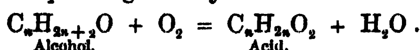
The true chemical definition of an alcohol of this series rests upon the circumstance, that under the influence of oxidising agents, it first parts with two atoms of hydrogen, and is converted into an *aldehyde* (alcohol dehydrogenated), and afterwards absorbs an atom of oxygen, yielding an acid. Thus, it has been already shown (p. 487), that vinic alcohol (C_2H_6O), when exposed to air under favourable conditions, yields aldehyde, C_2H_4O, which, by absorbing oxygen, is converted into acetic acid, $C_2H_4O_2$.

The formation of an aldehyde would, therefore, be represented by the general formula—



$$\underset{\text{Alcohol.}}{C_nH_{2n+2}O} + O = \underset{\text{Aldehyde.}}{C_nH_{2n}O} + H_2O,$$

and that of the corresponding acid by



$$\underset{\text{Alcohol.}}{C_nH_{2n+2}O} + O_2 = \underset{\text{Acid.}}{C_nH_{2n}O_2} + H_2O.$$

* This alcohol is of recent discovery, and has been little examined.

In addition to this, a double molecule of each of these alcohols, by the loss of the elements of a molecule of water, yields an *ether*, corresponding to ordinary ether $(C_2H_5)_2O$, which differs from the double molecule of vinic alcohol, C_2H_6O, by the elements of a molecule of water.

The general formula representing the derivation of an ether from an alcohol of the above series is—



$$\underset{\text{Alcohol.}}{2C_nH_{2n+2}O} - H_2O = \underset{\text{Ether.}}{(C_nH_{2n+1})_2O}.$$

Hence every alcohol has its corresponding aldehyde, acid, and ether, so that there are homologous series of aldehydes, acids and ethers, just as of the alcohols from which they are derived.

The only members of the aldehyde and ether series which have received a large share of attention on account of their practical importance, are those derived from ordinary alcohol; but the series of acids contains many members of importance, to some of which no corresponding alcohols are yet known.

The very important homologous series of acids* composed after the general formula $C_nH_{2n}O_2$, includes—

Acid.	Source.	Formula.
1. Formic acid,	Red ants, nettles	CH_2O_2
2. Acetic ,,	Vinegar	$C_2H_4O_2$
3. Propylic ,,	Oxidation of oils	$C_3H_6O_2$
4. Butyric ,,	Rancid butter	$C_4H_8O_2$
5. Valerianic acid	Valerian root	$C_5H_{10}O_2$
6. Caproic ,,	Rancid butter	$C_6H_{12}O_2$
7. Œnanthic ,,	Oxidation of castor oil	$C_7H_{14}O_2$
8. Caprylic ,,	Rancid butter	$C_8H_{16}O_2$
9. Pelargonic acid	Geranium leaves	$C_9H_{18}O_2$
10. Rutic or capric acid	Rancid butter	$C_{10}H_{20}O_2$
11. Euodic† ,,	Oil of rue	$C_{11}H_{22}O_2$
12. Lauric ,,	Bay berries	$C_{12}H_{24}O_2$
13. Cocinic ,,	Cocoa nut oil	$C_{13}H_{26}O_2$
14. Myristic ,,	Nutmeg butter	$C_{14}H_{28}O_2$
15. Benic ,,	Oil of ben	$C_{15}H_{30}O_2$
16. Palmitic ,,	Palm oil	$C_{16}H_{32}O_2$
17. Margaric ,,	Olive oil ?	$C_{17}H_{34}O_2$
18. Stearic ,,	Tallow	$C_{18}H_{36}O_2$
19. Balenic ,,		$C_{19}H_{38}O_2$
20. Butic ,,	Butter	$C_{20}H_{40}O_2$
21. Nardic ,,		$C_{21}H_{42}O_2$
27. Cerotic ,,	Bees' wax	$C_{27}H_{54}O_2$
30. Melissic ,,	Bees' wax	$C_{30}H_{60}O_2$

A very gradual transition of properties is observable in the members of this extended series of acids.

* Often spoken of as the *acetic series of acids*, or the *fatty acid series.*

† Εὐώδης, fragrant.

The first nine members of the series are liquid, the remainder solid at common temperatures. Of the liquids, formic acid boils at 221° F., and the boiling points of the other members exhibit a gradual rise up to pelargonic acid, which boils at 500° F. The melting-points of the solid acids also ascend from 86° F. for rutic acid ($C_{10}H_{20}O_2$) to 192° F. for melissic ($C_{30}H_{60}O_2$).

Formic and acetic acids may be mixed with water in all proportions, like their corresponding alcohols, the methylic and ethylic; propylic acid, though soluble to a great extent in water, resembles the corresponding alcohol in not mixing indefinitely with water. Butyric acid behaves in a similar manner. Valerianic, caproic, œnanthic, and caprylic acids are sparingly soluble in water. Pelargonic and capric acids are very sparingly soluble, and the remaining members of the series are very decidedly *fatty acids*, insoluble in water, and forming *soaps* with the alkalies.

The members of the series of alcohols, under the action of powerful dehydrating agents, are capable of parting with the elements of a molecule of water, furnishing the members of a homologous series of hydrocarbons related to their corresponding alcohols, as olefiant gas or ethylene (C_2H_4) is related to ethylic alcohol.

The general formula for the production of the homologues of ethylene (or *olefines*) from the alcohols may be thus expressed—



$$C_nH_{2n+2}O - H_2O = C_nH_{2n}.$$

The known members of this series of hydrocarbons are

Name.	Formula.	Corresponding Acid.	Corresponding Alcohol.
1. Methylene .	CH_2	Formic	Wood-naphtha
2. Ethylene .	C_2H_4	Acetic	Alcohol
3. Propylene .	C_3H_6	Propylic	Propylic
4. Butylene . .	C_4H_8	Butyric	Butylic
5. Amylene .	C_5H_{10}	Valerianic	Fousel oil
6. Caproylene .	C_6H_{12}	Caproic	Caproic
7. Œnanthene .	C_7H_{14}	Œnanthic	Œnanthic
8. Caprylene .	C_8H_{16}	Caprylic	Caprylic
9. Elaene . .	C_9H_{18}	Pelargonic	
10. Paramylene .	$C_{10}H_{20}$	Rutic	Rutic
16. Cetylene .	$C_{16}H_{32}$	Palmitic	Ethal
27. Cerotene .	$C_{27}H_{54}$	Cerotic	Cerotene
30. Melissene .	$C_{30}H_{60}$	Melissic	Melissine

Of these hydrocarbons, methylene, ethylene, and propylene are gaseous; butylene is also a gas, but easily condensed to a liquid state; the remainder are liquid at the ordinary temperature, except cerotene and melissene which are solid.

This series exhibits one of the best examples of *polymerism* or multiple relation of composition, each member of the series being represented by a formula which is a multiple by some whole number of that of the first member of the series.

Since one molecule of each of these hydrocarbons in the state of vapour occupies *two volumes*, it must follow, if their composition be correctly stated, that their vapour densities exhibit a multiple relation similar to that which exists between their formulæ.

That this is the case will be seen by the subjoined table, which illustrates very clearly the importance of determining the specific gravity of the vapour of a volatile substance as a confirmation of the results of analysis:—

Hydrocarbon.		Specific gravity of vapour
Methylene,	CH_2	0·490
Ethylene,	C_2H_4	0·978
Propylene,*	C_3H_6	1·498
Butylene,	C_4H_8	1·852
Amylene,	C_5H_{10}	2·386
Caproylene,	C_6H_{12}	2·875
Caprylene,	C_8H_{16}	3·90
Elaene,	C_9H_{18}	4·48
Paramylene	$C_{10}H_{20}$	5·061
Cetylene,	$C_{16}H_{32}$	8·007

It will be observed that just as the formula of cetylene ($C_{16}H_{32}$) is a multiple of that of methylene (CH_2) by 16, so, allowing for errors of experiment, the vapour density of cetylene (8·007) is 16 times that of methylene (0·490).

369. ALCOHOL may be studied as the type of the class to which it gives a name.

When any of the fermented or distilled liquors of commerce are subjected to distillation, the alcohol passes over during the first part of the process, mixed with a considerable quantity of water; and if the distillation be continued as long as any alcohol passes over, and the whole of the distilled liquid be measured or weighed, the quantity of alcohol present in the original liquid subjected to distillation, may be inferred (by reference to a table) from the specific gravity of the aqueous spirit distilled from it, since the lighter it is the more alcohol it contains, the specific gravity of pure alcohol being 0·794.

The strength of the spirit of wine of commerce is ascertained by determining its specific gravity. That known as *proof spirit* has the specific gravity 0·920, and is so called because it is the weakest spirit which will answer to the rough proof of firing gunpowder which has been moistened with it and kindled. Any spirit weaker than this leaves the powder moist, and does not explode it. It is then said to be *under proof*, whilst a stronger spirit is spoken of as *over proof.*

Proof spirit contains by weight, in 100 parts—

Water,	50·76
Alcohol,	49·24

A spirit would be spoken of as 30 per cent., for example, *over proof*, if 100 measures of it, when diluted with water, would yield 130 measures of proof spirit. A spirit 30 per cent. *below proof* contains, in every 100 measures, 70 measures of proof spirit. By repeatedly rectifying or re-

* These hydrocarbons are sometimes designated by names which refer to the multiple of CH_2 which they contain. Thus propylene, $3(CH_2)$, is sometimes called *tritylene*; butylene, *tetrylene*; caproylene, *hexylene*, &c.

distilling the weak spirit obtained from a fermented liquid, collecting the first portions separately, a strong spirit may be obtained, containing 90 per cent. of alcohol, but mere distillation will not effect a further separation of the water. Weak spirit may be concentrated to a greater extent than this, by leaving it enclosed in a bladder for a considerable period, when the water exudes through the bladder more readily than the alcohol, so that the latter accumulates in the mixture to the amount of 95 per cent.

Another method of separating a great part of the water consists in adding dry carbonate of potash to the weak spirit as long as it is dissolved, when the mixture separates into two layers, the lower consisting of solution of carbonate of potash in water, and the upper one of spirit, containing 89 per cent. of alcohol. By effecting the separation by means of carbonate of potash in a graduated tube, this method is sometimes employed for roughly ascertaining the proportion of alcohol in a fermented or distilled liquid, the foreign matters in which prevent any safe inference from the specific gravity.

The last portions of water are removed from alcohol by allowing it to stand for two or three days over powdered quick-lime, and distilling, when the lime retains the water in the form of hydrate of lime, and the pure or *absolute alcohol* distils over. It must then be preserved in well stopped bottles, since it readily absorbs moisture from the atmosphere. Its attraction for water causes it to evolve heat when mixed with that liquid, and the volume of the mixture is less than the sum of the volumes of its components, showing that combination has taken place.

370. ETHER, or, as it is sometimes erroneously called, *sulphuric ether* ($C_4H_{10}O$), is obtained by distilling a mixture of two measures of alcohol with one measure of concentrated sulphuric acid. As soon as the mixture begins to blacken, in consequence of a secondary decomposition of the alcohol, the retort is allowed to cool, another half measure of alcohol is added, and the mixture again distilled as long as ether is obtained.

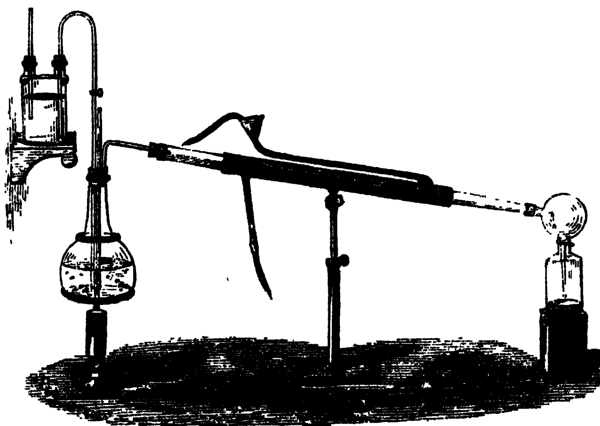


Fig. 292.—Continuous etherification.

A far better method of obtaining ether is that known as the *continuous process*. Alcohol of sp. gr. 0·830 is mixed with an equal measure of concentrated sulphuric acid, and introduced into a retort or flask (fig. 292),

which is connected with a small cistern containing alcohol. The mixture in the flask is rapidly raised to the boiling point, and alcohol is allowed to pass slowly in from the reservoir through a syphon furnished with a stop-cock, so as to keep the liquid in the flask at a constant level. A thermometer should be immersed in the liquid, the temperature of which should be maintained at 284° to 290° F. By this process, one measure of sulphuric acid will effect the conversion into ether of thirty measures of alcohol.

The boiling point of ether being very low (94°·8 F.) necessitates the employment of a good condensing arrangement in this process.

The liquid which distils over contains about two-thirds of its weight of ether, with about one-sixth of water, and an equal quantity of alcohol. Traces of sulphurous acid are also generally present. To obtain the pure ether, it is shaken with water containing a little carbonate of potash, when the water dissolves the alcohol, and the potash removes the sulphurous acid; the ether being very sparingly soluble in, and much lighter than water (sp. gr. 0·74), rises to the surface, holding a little water in solution. This upper layer is drawn off and freed from water by distillation in a water bath, at a very low heat, over quick-lime.

The explanation of the chemistry of this process of *etherification* will be more intelligible after some other changes to which alcohol is liable have been studied.

The most striking properties of ether are its peculiar odour and its great volatility; its rapid evaporation when poured upon the hand gives rise to a sensation of intense cold; and if a little ether be evaporated by blowing upon it in a watch-glass with a drop of water hanging from its convexity, the water will be speedily frozen. Ether is also exceedingly inflammable; and since its vapour is very heavy (sp. gr. 2·59), and passes in an unbroken stream through the air for a considerable distance, great care should be taken to avoid pouring it from a bottle in the neighbourhood of a flame. Its flame is far more luminous than that of alcohol, and much acetylene is produced during its imperfect combustion (p. 91).

The high specific gravity, volatility, and inflammability of ether vapour admit of illustration by some curious experiments :—

If a small piece of sponge be saturated with ether and placed in the centre of a large wooden tray, two or three inches deep, the latter will soon be entirely filled with the vapour, as may be shown by applying a lighted match to one corner. A jug may be warmed by rinsing a little hot water round it, and this having been thrown out, a few drachms of ether may be poured into the jug, which will immediately become filled with ether vapour, and from this several glasses may be filled in succession, the presence of the ether vapour being proved by a lighted taper.

A pneumatic trough may be filled with warm water, a small test-tube filled with ether inverted with its mouth under the water, and the ether quickly decanted up into a gas jar also filled with hot water, where it will be immediately converted into vapour, and may be decanted through the water into other vessels, and dealt with like a permanent gas. Some cold water poured over the jar containing it at once proves its condensible character.

When ether is acted upon by hydrochloric, hydrobromic, or hydriodic acid, the oxygen of the ether enters into combination with the hydrogen of the acid, and the chlorine, bromine, or iodine occupies its place.

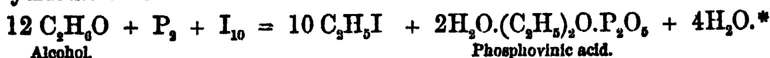
Thus, with hydrochloric acid—



$$(C_2H_5)_2O \text{ (Ether)} + 2HCl = 2C_2H_5Cl \text{ (Hydrochloric ether)} + H_2O.$$

In a similar manner, *hydrobromic ether*, C_2H_5Br, and *hydriodic ether*,

C_2H_5I, may be formed. The best method of obtaining the two last, however, consists in distilling moderately strong alcohol with phosphorus, and either bromine or iodine, when *phosphovinic* or *phosphethylic* acid and hydriodic ether are formed—



$$\underset{\text{Alcohol.}}{12\,C_2H_6O} + P_2 + I_{10} = 10\,C_2H_5I + \underset{\text{Phosphovinic acid.}}{2H_2O.(C_2H_5)_2O.P_2O_5} + 4H_2O.^{*}$$

These three ethers are colourless, fragrant, volatile liquids, which are of the greatest value in the investigation of the constitution of complex organic compounds.

This remark applies particularly to hydriodic ether (*iodide of ethyle*), which is less volatile than the others, and therefore more easily manageable in experiments requiring a high temperature.

Iodide of ethyle, or *ethylic iodide*, is prepared by distilling 1400 grains of ordinary alcohol (sp. gr. 0·84) with 2000 grains of iodine, and 100 grains of ordinary vitreous phosphorus. The iodine and phosphorus are added alternately, in small portions, to the alcohol in the retort, which is immersed in cold water to moderate the action, and occasionally shaken. When the whole has been added, the retort is connected with a Liebig's condenser, and heated in the water-bath, when about 2½ measured ounces of iodide of ethyle mixed with alcohol will pass over. This is shaken in a stoppered bottle with about an equal measure of water, which dissolves the alcohol, leaving the iodide of ethyle to collect at the bottom as an oily layer (sp. gr. 1·97). After as much as possible of the upper aqueous layer has been removed with a siphon or pipette, the iodide is poured into a small retort containing fused chloride of calcium in powder to remove the water. The retort is closed with a cork, and set aside for some hours, when the iodide of ethyle may be distilled off in the water-bath, and condensed in a Liebig's condenser.

371. ALCOHOL-RADICALS.—If ethylic iodide be poured over granulated zinc contained in a stout glass tube, which is then exhausted of air, hermetically sealed, and heated for two hours in an oil-bath to 300° F., a crystalline substance is deposited, which is a compound of iodide of zinc with zinc-ethyle $(C_2H_5)_2Zn$, whilst a colourless liquid separates, consisting of a mixture of three hydrocarbons, which have been liquefied by their own pressure. On breaking the extremity of the tube under water, this liquid rapidly escapes in the form of gas, which proves on examination to contain olefiant gas (C_2H_4), hydride of ethyle (C_2H_6), and ethyle $(C_2H_5)_2$, the last of which may be obtained nearly pure by collecting the last portions of gas separately, since ethyle is the least volatile of these hydrocarbons.

Neglecting the secondary decompositions which give rise to the other products, the formation of ethyle would be represented by the simple equation—



$$\underset{\text{Ethylic iodide.}}{2C_2H_5I} + Zn = ZnI_2 + \underset{\text{Ethyle.}}{(C_2H_5)_2}$$

Ethyle is a colourless gas, having a faint ethereal smell, insoluble in water, and requiring a pressure of two or three atmospheres for its liquefaction. The interest which attaches to it is due to its being regarded by many chemists as the radical or starting-point of the series of compounds derived from vinic alcohol, which is thence spoken of as the ethyle series, and this view of the constitution of those compounds was in favour long before the compound $(C_2H_5)_2$ was obtained in the separate state, this being a discovery of recent date.

* It will be seen that this change is precisely similar to that which occurs in the preparation of hydriodic acid by the simultaneous action of phosphorus and iodine upon water—

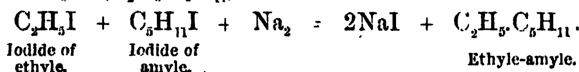


$$12\,H_2O + P_2 + I_{10} = 10\,HI + 2H_2O.H_2O.P_2O_5 + 4H_2O.$$

Mention has already been made of the existence of another radical, methyle $(CH_3)_2$, obtained by a similar process, which may be regarded as the starting-point of the wood-spirit series.

Butyle $(C_4H_9)_2$, *amyle* $(C_5H_{11})_2$, and *caproyle* $(C_6H_{13})_2$ the supposed radicals of the butylic, amylic, and caproic alcohols, have also been obtained, these being liquids with progressive boiling points. We are thus in possession of several members of a homologous series of hydrocarbons, which may be designated the *alcohol-radicals*, and represented by the general formula $(C_nH_{2n+1})_2$.

If a mixture of iodide of ethyle and iodide of amyle ($C_5H_{11}I$, prepared from fousel oil just as iodide of ethyle is from alcohol) be heated with sodium, a colourless liquid is obtained, which is a true combination of ethyle and amyle $(C_2H_5.C_5H_{11})$—



$$C_2H_5I + C_5H_{11}I + Na_2 = 2NaI + C_2H_5.C_5H_{11}.$$

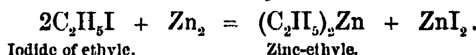
Iodide of ethyle. Iodide of amyle. Ethyle-amyle.

In a similar manner, ethyle-butyle $(C_2H_5.C_4H_9)$, methyle-caproyle $(CH_3.C_6H_{13})$, butyle-amyle $(C_4H_9.C_5H_{11})$, and butyle-caproyle $(C_4H_9.C_6H_{13})$, have been obtained.

These double radicals all yield two volumes of vapour for each molecule of the compound, showing that the empirical formula for methyle (CH_3), which furnishes only one volume, must be converted into that of a double radical, methyle-methyle $(CH_3.CH_3)$, which would give two volumes of vapour, and in a similar manner, ethyle would become (C_2H_5,C_2H_5), butyle (C_4H_9,C_4H_9), and so on.

This duplicate nature of the radicals at once explains the circumstance that they do not unite directly with chlorine, bromine, &c., as might have been expected. Thus ethyle, with iodine, does not combine to form iodide of ethyle, because the ethyle itself is an ethylide of ethyle.

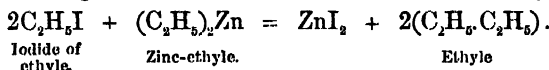
Again, the formation of zinc ethyle $(C_2H_5)_2Zn$, and of hydride of ethyle (C_2H_5H), during the action of zinc upon iodide of ethyle, becomes intelligible upon this view. Indeed, the first stage of this action appears to consist in the formation of zinc-ethyle—



$$2C_2H_5I + Zn_2 = (C_2H_5)_2Zn + ZnI_2.$$

Iodide of ethyle. Zinc-ethyle.

In the second stage, the zinc-ethyle acts upon a fresh portion of iodide of ethyle, producing iodide of zinc and the double radical ethyle—



$$2C_2H_5I + (C_2H_5)_2Zn = ZnI_2 + 2(C_2H_5.C_2H_5).$$

Iodide of ethyle. Zinc-ethyle. Ethyle

The hydride of ethyle itself clearly corresponds to the double radical ethyle, one-half of which is replaced by an atom of hydrogen $(C_2H_5.H)$.

The simultaneous formation of hydride of ethyle and of olefiant gas during the action of zinc upon iodide of ethyle, might be represented by the equation—



$$2C_2H_5I + Zn_2 = ZnI_2 + C_2H_5.H + C_2H_4.$$

Iodide of ethyle. Hydride of ethyle.

Hydride of ethyle is the representative of a series of homologous hydrocarbons, of which the first member, the hydride of methyle $(CH_3.H)$, is identical with marsh-gas.

The following table exhibits some of the chief members of the marsh-

gas series of hydrocarbons (general formula C_nH_{2n+2}), as well as the corresponding alcohol-radicals,* having the general formula $2(C_nH_{2n+1})$—

	Radical.	Hydride.†
Methyle, . .	$CH_3.CH_3$	$CH_3.H = CH_4$
Ethyle, . .	$C_2H_5.C_2H_5$	$C_2H_5.H = C_2H_6$
Butyle, . .	$C_4H_9.C_4H_9$	$C_4H_9.H = C_4H_{10}$
Amyle, . .	$C_5H_{11}.C_5H_{11}$	$C_5H_{11}.H = C_5H_{12}$

The three first of these hydrides are gaseous, the last a volatile liquid.

If ethyle $(C_2H_5)_2 = E_2$ be accepted as the radical of the alcohol series, then ether $(C_2H_5)_2O$ would become the oxide of ethyle, and alcohol (C_2H_5HO), the hydrate of ethyle; and it will be seen that upon this view a considerable number of the relations of these bodies can be readily explained.

372. On referring to the action of hydrochloric acid upon ether, it will be seen to resemble exactly that of the same acid upon the basic oxide of a metal, consisting in an exchange between the chlorine of the acid and the oxygen of the base. Chloride of ethyle may also be produced by the action of hydrochloric acid upon alcohol (EHO), just as chloride of potassium is produced by the action of that acid upon caustic potash—

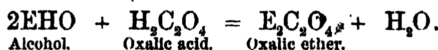


$$\text{EHO}\ (\textit{Alcohol}) + \text{HCl} = \text{ECl}\ (\textit{Chloride of ethyle}) + H_2O.$$

It would be expected that the action of other acids upon alcohol would correspond to their action upon caustic potash, and with several acids this is really the case, although it is far more difficult to break up the alcohol than the caustic potash.

If alcohol be boiled for many hours with dry oxalic acid $(H_2C_2O_4)$ in a flask provided with a long tube, so that the volatilised alcohol may run back, it is found that, on diluting the solution with water, a heavy fragrant liquid separates, which has the composition $(C_2H_5)_2C_2O_4$, and is termed *oxalic ether*.

Its formation may be thus represented—



$$\underset{\text{Alcohol.}}{2EHO} + \underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Oxalic ether.}}{E_2C_2O_4} + H_2O.$$

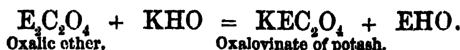
It is formed far more easily in the presence of strong sulphuric acid, since this developes ether (E_2O) which is decomposed by the oxalic acid.

By treatment with caustic potash, the oxalic ether is decomposed, yielding oxalate of potash and alcohol; thus—



$$E_2C_2O_4 + 2KHO = K_2C_2O_4 + 2EHO.$$

But if oxalic ether be mixed with only half the quantity of caustic potash required for this decomposition, there is obtained, instead of oxalate of potash, a salt, crystallising in pearly scales, having the composition KEC_2O_4, the formation of which is easily understood—



$$\underset{\text{Oxalic ether.}}{E_2C_2O_4} + KHO = \underset{\text{Oxalovinate of potash.}}{KEC_2O_4} + EHO.$$

By decomposing this salt with hydrofluosilicic acid (see p. 185) to remove the potassium in an insoluble form, a new acid is obtained, which has the composition HEC_2O_4, and is called *oxalovinic* or *oxalethylic acid.* It

* See also American petroleum, p. 463.

† Each of these hydrides is isomeric with the radical immediately preceding it. Thus hydride of ethyle has the same composition as methyle, and is regarded by some chemists as identical with it.

might evidently be also called the binoxalate of ethyle, since it corresponds in composition to the binoxalate of potash, KHC_2O_4.

Most of the acids form ethers corresponding to oxalic ether; thus, by distilling acetic acid with alcohol and sulphuric acid, and diluting the distilled liquid with water, *acetic ether* ($EC_2H_3O_2$) is separated, remarkable for its very fragrant odour, which has a share in the perfume of cider, perry, vinegar, and of many wines.

The ether used in medicine under the names of *sweet spirits of nitre, nitrous ether*, and *nitric ether*, is essentially a solution of nitrous ether $(C_2H_5)NO_2$ in alcohol, and is formed when alcohol is distilled with nitric acid, when a violent and complicated reaction takes place, one portion of the alcohol being converted into aldehyde, at the expense of a part of the oxygen of the nitric acid—



$$\underset{\text{Alcohol.}}{2(C_2H_6O)} + HNO_3 = \underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Nitrous ether.}}{C_2H_5NO_2} + 2H_2O.$$

Nitrous ether is a very volatile liquid, characterised by a powerful odour of rennet-apples, and in the pure state decomposes spontaneously, evolving nitric oxide.

True *nitric ether* (ENO_3) may also be obtained as a fragrant, heavy oily liquid, by distilling alcohol with nitric acid, under certain precautions. It is decomposed with explosion at a temperature of about 200° F.

By the action of nascent hydrogen upon nitric ether, a basic substance is produced, which has been named *hydroxylamine*, in allusion to its remarkable formula, NH_3O, which might be regarded as ammonia, NH_3, in which one atom of hydrogen is replaced by *hydroxyle*, HO—



$$\underset{\text{Nitric ether.}}{C_2H_5NO_3} + H_6 = \underset{\text{Alcohol.}}{C_2H_5HO} + H_2O + \underset{\text{Hydroxylamine.}}{NH_3O}.$$

In order to obtain this base, 5 parts of nitric ether are acted on by 12 parts of tin and 50 parts of concentrated hydrochloric acid. When the action is over, the alcohol is expelled by heat, the tin precipitated by hydrosulphuric acid, the solution evaporated to dryness, and the residue boiled with absolute alcohol, which leaves some hydrochlorate of ammonia undissolved. The *hydrochlorate of hydroxylamine* ($NH_3O.HCl$) crystallises in long needles from the alcoholic solution. From the sulphate of hydroxylamine, by decomposition with baryta, a solution of the base itself may be obtained; but pure hydroxylamine has not been isolated from the solution, since it has a tendency to decompose into ammonia, water, and nitrogen—



$$\underset{\text{Hydroxylamine.}}{3NH_3O} = NH_3 + N_2 + 3H_2O.$$

Hydroxylurea $CH_3(HO)N_2O$, or urea in which hydrogen is replaced by hydroxyle, has also been obtained.

The *chloric ether* used for medicinal purposes is not an ether in the true sense of the term, but a solution of chloroform ($CHCl_3$) in alcohol. Chloroform will be more particularly described hereafter.

Perchloric ether, $(C_2H_5)ClO_4$, is only interesting from the circumstance that, although an oily liquid, it explodes violently under a sudden blow.

Boracic ether, which has the formula E_3BO_3, is formed when terchloride of boron is decomposed by alcohol—



$$BCl_3 + 3(EHO) = E_3BO_3 + 3HCl,$$

and may also be obtained by heating anhydrous boracic acid with an excess of alcohol under pressure. It is lighter than water (sp. gr. 0·88), and boils at 246° F. When heated with anhydrous boracic acid, it is converted into $E_2O.B_2O_3$, which is decomposed by heat into E_3BO_3 and $E_2O.3B_2O_3$, the latter being a vitreous solid.

When chloride of silicon is decomposed by alcohol, the compound $2E_2O.SiO_2$ is produced—



$$SiCl_4 + 4(EHO) = 2E_2O.SiO_2 \text{ (Silicic ether)} + 4HCl.$$

This *silicic ether* is a colourless liquid, of sp. gr. 0·93, and distilling unchanged at

330° F. It has an ethereal odour, and burns with a brilliant flame which deposits silica. When poured upon the surface of water, it gradually decomposes, with separation of gelatinous hydrated silica—



$$2E_2O.SiO_2 + 2H_2O = 4(EHO) \text{ (Alcohol)} + SiO_2 .$$

When the ether is kept in a moist atmosphere, it deposits a hard transparent mass of silica, known as *artificial quartz.*

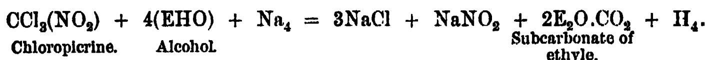
Two other silicic ethers have been obtained, having respectively the composition $E_2O.SiO_2$ and $E_2O.2SiO_2$; the former liquid, the latter viscous.

Carbonic ether ($E_2O.CO_2$) may be obtained by heating carbonate of silver with iodide of ethyle in a sealed tube;



$$Ag_2O.CO_2 + 2EI = E_2O.CO_2 + 2AgI .$$

The compound $2E_2O.CO_2$ has been obtained by the action of sodium upon an alcoholic solution of chloropicrine—



$$\underset{\text{Chloropicrine.}}{CCl_3(NO_2)} + \underset{\text{Alcohol.}}{4(EHO)} + Na_4 = 3NaCl + NaNO_2 + \underset{\text{Subcarbonate of ethyle.}}{2E_2O.CO_2} + H_4 .$$

When carbonic acid is passed through a solution of hydrate of potash in absolute alcohol, the *carbovinate of potash* is obtained, in crystals having the composition $KECO_3$, corresponding to bicarbonate of potash, $KHCO_3$.

By the action of syrupy phosphoric acid upon alcohol, the compound $2H_2O.E_2O.P_2O_5$, *phosphovinic acid*, is formed, and by neutralising it with a base, a *phosphovinate* may be obtained, composed after the general formula $2M_2'O.E_2O.P_2O_5$.

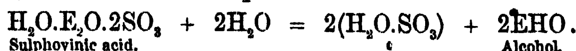
A second acid is formed at the same time, having the formula $H_2O.2E_2O.P_2O_5$, its salts being $M_2'O.2E_2O.PO_5$. Phosphovinic acid is found abundantly in the residue from the preparation of iodide of ethyle.

The true phosphoric ether ($3E_2O.P_2O_5$) is also said to have been obtained.

The true *sulphuric ether* ($E_2O.SO_3$) can only be formed by passing the vapour of anhydrous sulphuric acid into ether. It is an oily liquid, heavier than water, and decomposed by heat, olefiant gas and alcohol being found amongst the products, for $C_2H_4 + C_2H_6O = (C_2H_5)_2O$.

The fragrant liquid known as *heavy oil of wine*, which is formed towards the latter part of the preparation of ether and of olefiant gas (page 92), appears to contain the sulphate of oxide of ethyle, together with some hydrocarbons of the olefiant gas series. When decomposed with a solution of potash, *light oil of wine* rises, which contains hydrocarbons of the olefiant gas series.

373. When ether or alcohol is added to concentrated sulphuric acid, much heat is evolved, in consequence of the combination of the oxide of ethyle with sulphuric acid, to form *sulphovinic* or *sulphethylic acid*, $H_2O.E_2O.2SO_3$ or bisulphate of oxide of ethyle, corresponding in composition to the bisulphate of potash, $K_2O.H_2O.2SO_3$. If baryta be now added to the solution, the uncombined sulphuric acid will be precipitated in the form of sulphate of baryta, but the sulphovinic acid will combine with the base to form the sulphovinate of baryta, which may be obtained by evaporating the solution, in rhombic prisms which have the formula $BaO.E_2O.2SO_3.2Aq.$, and are easily soluble in water. By cautiously adding sulphuric acid to the solution of sulphovinate of baryta till the whole of the baryta is precipitated as sulphate, and evaporating the filtered liquid *in vacuo*, the pure sulphovinic acid is obtained as a syrupy liquid liable to spontaneous decomposition, and readily decomposed when heated with water, into alcohol and sulphuric acid—



$$\underset{\text{Sulphovinic acid.}}{H_2O.E_2O.2SO_3} + 2H_2O = 2(H_2O.SO_3) + \underset{\text{Alcohol.}}{2EHO} .$$

The sulphovinate of soda, prepared by decomposing the baryta-salt with carbonate of soda, is used medicinally in Germany.

374. *Vinic acids are not formed by monobasic acids.*—It must be noticed that although the greater number of the acids are capable of forming ethers,

only a few of them produce vinic acids. Indeed, only those acids form vinic acids which are polybasic, *i.e.*, require more than one atom of a metal for the formation of a normal salt (p. 254), the tendency to form a vinic acid depending upon the possibility of replacing a portion of the hydrogen in the hydrated acid by ethyle. In the case of nitric acid, which is undoubtedly a monobasic acid, and does not form acid salts, no vinic acid can be produced; the formula of the acid being HNO_3, the hydrogen must be *entirely* or not at all replaced by the ethyle.

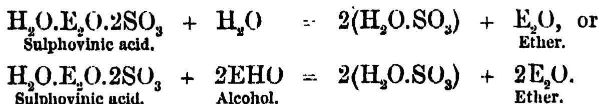
375. *Theory of etherification.*—When sulphovinic acid is decomposed by heat, especially in the presence of excess of alcohol, a large proportion of ether is found among the products, and this has given rise to a very general opinion among chemists, that the production of sulphovinic acid is an intermediate stage in the formation of ether, by the ordinary process of distilling alcohol with sulphuric acid. At first sight it would appear that the etherification of alcohol in this process was sufficiently explained by reference to the attraction of sulphuric acid for water, and consisted in a simple removal of water from the alcohol by the acid, for—



$$\underset{\text{Alcohol.}}{2C_2H_6O} - H_2O = \underset{\text{Ether.}}{C_4H_{10}O}.$$

When it is found, however, that a continuous stream of alcohol, flowing into heated sulphuric acid in a retort, is converted into ether and water, which is not retained by the sulphuric acid, but distils over with the ether, and that this may go on almost without limit, this explanation is no longer tenable.

Accordingly, the formation of ether from alcohol by the action of sulphuric acid is generally referred to the formation of sulphovinic acid, as soon as the alcohol and the acid are brought in contact, and the subsequent decomposition of this sulphovinic acid, in the presence of water or alcohol, into hydrated sulphuric acid, water, and ether; thus—



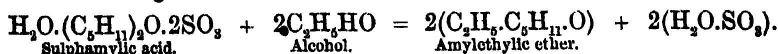
$$\underset{\text{Sulphovinic acid.}}{H_2O.E_2O.2SO_3} + H_2O = 2(H_2O.SO_3) + \underset{\text{Ether.}}{E_2O}, \text{ or}$$

$$\underset{\text{Sulphovinic acid.}}{H_2O.E_2O.2SO_3} + \underset{\text{Alcohol.}}{2EHO} = 2(H_2O.SO_3) + \underset{\text{Ether.}}{2E_2O}.$$

The hydrated sulphuric acid thus set free would of course give rise to the formation of a fresh quantity of sulphovinic acid, which would be decomposed in its turn, and so on without limit.

A strong argument in favour of this view is deducible from the following experiment:—

When amylic alcohol (the amylic hydrate $C_5H_{11}HO$) is mixed with concentrated sulphuric acid, it forms sulphamylic acid $(C_5H_{11})_2O.H_2O.2SO_3$, corresponding to sulphovinic acid, and if this be heated in a retort, and alcohol be allowed to flow into it, as in making ether, the first portion which distils over is found to be a true *double ether molecule* $(C_2H_5.C_5H_{11}.O)$, the production of which would be represented by the equation—



$$\underset{\text{Sulphamylic acid.}}{H_2O.(C_5H_{11})_2O.2SO_3} + \underset{\text{Alcohol.}}{2C_2H_5HO} = \underset{\text{Amylethylic ether.}}{2(C_2H_5.C_5H_{11}.O)} + 2(H_2O.SO_3).$$

On continuing the distillation, nothing but ordinary ethylic ether is obtained.

The existence of these double ethers might have been anticipated from what has been said with respect to the double radicals (p. 513), but the

mode of formation in the above instance certainly affords support to the view, that ether results from the decomposition of sulphovinic acid by alcohol in the ordinary etherifying process.

On the other hand, this theory of etherification is shaken by the circumstance, that if vapour of alcohol be passed into boiling sulphuric acid, of sp. gr. 1·52 (boiling at 290°) almost the whole of the alcohol is resolved into water and ether, which distil over, so that either no sulphovinic acid is formed, or it is only formed to be immediately decomposed. If the acid have the sp. gr. 1·61 (boiling at 330°), no ether is obtained, the alcohol being resolved into olefiant gas and water.

Moreover, hydrated phosphoric acid cannot be substituted for the sulphuric acid in the preparation of ether, notwithstanding that it also forms a vinic acid.

Hence, many chemists are inclined to attribute to sulphuric acid a specific action by contact (*catalytic action*) upon alcohol, causing its resolution into water and ether, or olefiant gas, according to the temperature.

This view receives some confirmation from the behaviour of sulphuric acid towards cellulose and certain other substances, in which it causes important transformations, without itself appearing to take part in the change.

In connection with this subject, it is remarkably interesting to observe, that alcohol may actually be reproduced from olefiant gas and water under the influence of sulphuric acid. If concentrated sulphuric acid be violently agitated in a vessel containing olefiant gas, the latter is absorbed, and on diluting the acid with water and distilling, a quantity of alcohol is obtained.

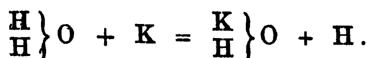
376. *Alcohols and ethers referred to the water-type.*—When potassium or sodium is thrown into absolute alcohol, the metal is dissolved with disengagement of heat and rapid evolution of hydrogen, and a crystalline compound is formed, known as *potassium-alcohol* (*ethylate of potash*) or *sodium-alcohol* (*ethylate of soda*), and containing an atom of the metal in the place of an atom of hydrogen; the action of potassium upon alcohol would be thus represented—



$$C_2H_5HO \text{ (Alcohol)} + K = C_2H_5KO \text{ (Potassium-alcohol)} + H.$$

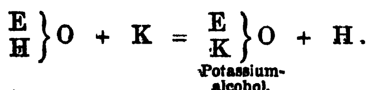
Other alcohols behave in a similar manner. No one can fail to be struck with the similarity which exists between the action of potassium upon alcohol and upon water, and chemists have naturally endeavoured to refer both actions to a common type.

The decomposition of water by potassium is represented by the equation—



$$\left.\begin{matrix}H\\H\end{matrix}\right\}O + K = \left.\begin{matrix}K\\H\end{matrix}\right\}O + H.$$

Alcohol may be represented with equal fitness, as water in which half the hydrogen is replaced by ethyle (C_2H_5), or EHO, and the action of potassium upon it may be thus expressed—



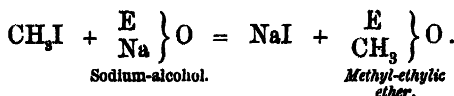
$$\left.\begin{matrix}E\\H\end{matrix}\right\}O + K = \left.\begin{matrix}E\\K\end{matrix}\right\}O + H.$$

Potassium-alcohol.

In a similar manner sodium-alcohol would be formed.*

When sodium-alcohol is heated in a sealed tube with the iodide of one of the alcohol-radicals, the sodium combines with the iodine, whilst the alcohol-radical enters into the place of the sodium, and a double ether is formed.

Thus, if iodide of methyle (CH_3I) be decomposed by sodium-alcohol—

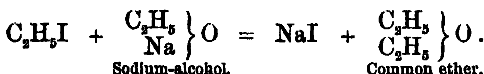


$$CH_3I + \left.\begin{matrix}E\\Na\end{matrix}\right\}O = NaI + \left.\begin{matrix}E\\CH_3\end{matrix}\right\}O.$$

Sodium-alcohol. *Methyl-ethylic ether.*

In a similar manner *amyl-ethylic ether*, $\left.\begin{matrix}E\\C_5H_{11}\end{matrix}\right\}O$, would be produced.

Again, if iodide of ethyle be decomposed by sodium-alcohol, common ether is obtained, and the action must in consistency be similarly explained—



$$C_2H_5I + \left.\begin{matrix}C_2H_5\\Na\end{matrix}\right\}O = NaI + \left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O.$$

Sodium-alcohol. Common ether.

Alcohol and ether are constituted upon the same type, that of a molecule of water, and bear to each other the same relation as exists between caustic potash and potash; thus—

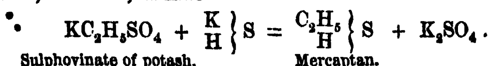
Potassium series.		Ethyle series.	
Potassium,	K_2	$(C_2H_5)_2$	Ethyle.
Caustic potash,	$\left.\begin{matrix}K\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	Alcohol.
Potash,	$\left.\begin{matrix}K\\K\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	Ether.

377. Compounds have been obtained corresponding to alcohol and ether, in which the place of the oxygen is occupied by sulphur, and which bear the same relation to hydrosulphuric acid as alcohol and ether bear to water.

Type.—Hydrosulphuric acid, $\left.\begin{matrix}H\\H\end{matrix}\right\}S$

Hydrosulphuric ether, (sulphide of ethyle),	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S$	Sulphide of potassium,	$\left.\begin{matrix}K\\K\end{matrix}\right\}S$
Mercaptan,	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$	Hydrosulphate of potassium,	$\left.\begin{matrix}K\\H\end{matrix}\right\}S.$

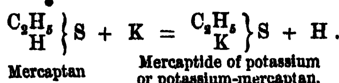
All these compounds are distinguished for their powerful odour of garlic. This is especially the case with mercaptan, which is notoriously one of the most evil-smelling chemical compounds. It is prepared by distilling solution of hydrosulphate of potassium (obtained by saturating potash with hydrosulphuric acid) with sulphovinate of potash, or better, of lime—



$$KC_2H_5SO_4 + \left.\begin{matrix}K\\H\end{matrix}\right\}S = \left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S + K_2SO_4.$$

Sulphovinate of potash. Mercaptan.

Mercaptan is a light, very volatile and inflammable liquid, sparingly soluble in water. That it is constituted after the type of hydrosulphuric acid is shown by its action upon metals and their oxides. Potassium acts upon it precisely as it does upon alcohol—

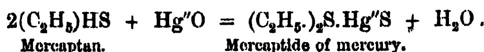


$$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S + K = \left.\begin{matrix}C_2H_5\\K\end{matrix}\right\}S + H.$$

Mercaptan. Mercaptide of potassium or potassium-mercaptan.

* Thallium-alcohol, C_2H_5TlO, has also been obtained as a colourless liquid remarkable for its high specific gravity (3·55) and great refractive and dispersive action upon light.

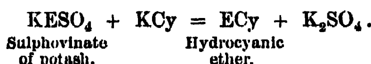
Its name was bestowed in allusion to its action upon mercuric oxide, when it forms a white crystalline inodorous compound, insoluble in water but soluble in alcohol—



$$2(C_2H_5)HS + Hg''O = (C_2H_5.)_2S.Hg''S + H_2O.$$

Mercaptan. Mercaptide of mercury.

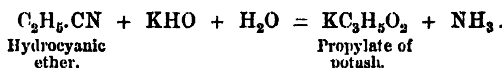
378. *Hydrocyanic ether* ($C_2H_5.CN$ = ECy), or cyanide of ethyle, is obtained by distilling sulphovinate of potash with cyanide of potassium—



$$KESO_4 + KCy = ECy + K_2SO_4.$$

Sulphovinate of potash. Hydrocyanic ether.

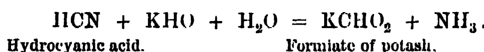
The cyanide of ethyle is a volatile poisonous liquid, smelling strongly of garlic. Its most interesting feature is, that when boiled with a solution of potash, it furnishes propylate of potash, whilst ammonia is evolved—



$$C_2H_5.CN + KHO + H_2O = KC_3H_5O_2 + NH_3.$$

Hydrocyanic ether. Propylate of potash.

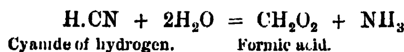
In a similar manner, the cyanides of all the alcohol-radicals, when boiled with solution of potash, yield the potash-salt of the acid which stands next in the homologous series. Thus cyanide of *methyle* ($CH_3.CN$) yields the potash-salt of acetic acid belonging to the *ethyle* series; cyanide of *amyle* ($C_5H_{11}.CN$) yields caproate of potash belonging to the *caproyle* series, and so on. This mode of decomposition argues strongly that hydrogen is really the type of these radicals, for when hydrocyanic acid (HCN) is boiled with solution of potash, it yields the potash-salt of formic acid, the lowest member of the homologous series—



$$HCN + KHO + H_2O = KCHO_2 + NH_3.$$

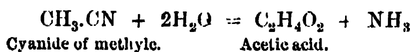
Hydrocyanic acid. Formiate of potash.

Thus, leaving the potash out of consideration;



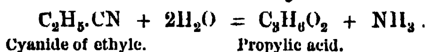
$$H.CN + 2H_2O = CH_2O_2 + NH_3$$

Cyanide of hydrogen. Formic acid.



$$CH_3.CN + 2H_2O = C_2H_4O_2 + NH_3$$

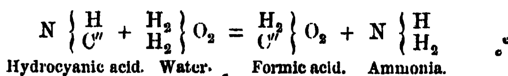
Cyanide of methyle. Acetic acid.



$$C_2H_5.CN + 2H_2O = C_3H_6O_2 + NH_3.$$

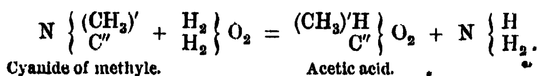
Cyanide of ethyle. Propylic acid.

A plausible explanation of these changes may be given, if the hydrocyanic acid (HCN) be represented as ammonia (NH_3), in which two atoms of hydrogen are replaced by an atom of carbon (just as two atoms of hydrogen in water are replaced by one atom of carbon to form carbonic oxide).



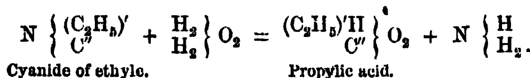
$$N\left\{\begin{matrix}H\\C''\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}H_2\\C''\end{matrix}\right\}O_2 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right.$$

Hydrocyanic acid. Water. Formic acid. Ammonia.



$$N\left\{\begin{matrix}(CH_3)'\\C''\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}(CH_3)'H\\C''\end{matrix}\right\}O_2 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right..$$

Cyanide of methyle. Acetic acid.



$$N\left\{\begin{matrix}(C_2H_5)'\\C''\end{matrix}\right. + \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 = \left.\begin{matrix}(C_2H_5)'H\\C''\end{matrix}\right\}O_2 + N\left\{\begin{matrix}H\\H_2\end{matrix}\right..$$

Cyanide of ethyle. Propylic acid.

The cyanides of the alcohol-radicals will be again referred to under their other designation of *nitriles*.

KAKODYLE SERIES—ORGANO-METALLIC BODIES.

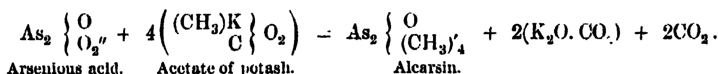
379. One of the most pleasing results of the progress of investigation in chemistry, is the discovery of the true position among classified compounds which is to be assigned to some substance hitherto regarded as anomalous, and as destroying by its presence the symmetry and completeness of an otherwise perfect classification. Such was the case, until within the last few years, with *kakodyle*, and the bodies derived from it. Discovered long before the science of organic chemistry was prepared to receive it, it taxed the ingenuity of chemists to find a place for it in their arrangement of organic compounds, and always occupied an anomalous and isolated position. Modern research has now brought to light a whole series of compounds, which would not have been complete without kakodyle, and this hitherto incomprehensible substance has at length been assigned its proper place.

When a mixture of equal weights of arsenious acid and dry acetate of potash is submitted to distillation, a heavy poisonous liquid is obtained, which has a most disgusting odour of garlic, and takes fire spontaneously when exposed to the air. This liquid, which has long been known under the names of *alcarsin* (arsenical alcohol), and *Cadet's fuming liquor*, has the composition $C_4H_{12}As_2O$, and its production may be represented (if the various secondary products be neglected) by the equation—



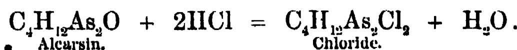
$$\underset{\text{Acetate of potash.}}{4(KC_2H_3O_2)} + As_2O_3 = \underset{\text{Alcarsin.}}{C_4H_{12}As_2O} + 2(K_2O.CO_2) + 2CO_2.$$

If acetic acid be represented by the formula derived above (p. 520) from its formation in the action of water upon cyanide of methyle, the formation of alcarsin would be easily explained. Acetate of potash would then be represented by the formula $\left.\begin{matrix}(CH_3)K\\C\end{matrix}\right\} O_2$, and its action upon arsenious acid might be thus expressed—



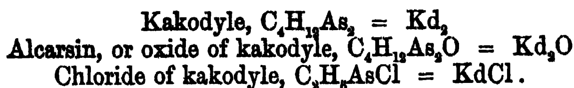
$$\underset{\text{Arsenious acid.}}{As_2\left\{\begin{matrix}O\\O_2''\end{matrix}\right.} + \underset{\text{Acetate of potash.}}{4\left(\left.\begin{matrix}(CH_3)K\\C\end{matrix}\right\} O_2\right)} = \underset{\text{Alcarsin.}}{As_2\left\{\begin{matrix}O\\(CH_3)'_4\end{matrix}\right.} + 2(K_2O.CO_2) + 2CO_2.$$

Alcarsin has the properties of a base; it is capable of combining with the oxygen acids to form crystallisable salts, and in contact with the hydrogen acids it furnishes water, together with a salt of the radical of the acid. Thus, with hydrochloric acid, we have—



$$\underset{\text{Alcarsin.}}{C_4H_{12}As_2O} + 2HCl = \underset{\text{Chloride.}}{C_4H_{12}As_2Cl_2} + H_2O.$$

The best method of obtaining this chloride consists in dissolving the alcarsin in alcohol, and adding an alcoholic solution of corrosive sublimate, when a white crystalline solid is obtained, composed of $C_4H_{12}As_2O.HgCl_2$; and on distilling this with hydrochloric acid (out of contact with air), another spontaneously inflammable liquid is obtained, of insupportable odour, and composed of C_2H_6AsCl. By distilling this chloride with zinc in an atmosphere of carbonic acid gas, a third unbearable liquid is procured, which has the formula $C_4H_{12}As_2$, and has been named *kakodyle*, in allusion to its intolerable odour (*κακός*, *bad*). This substance is obviously the radical from which the compounds just mentioned are immediately derived; thus—



Kakodyle, $C_4H_{12}As_2 = Kd_2$
Alcarsin, or oxide of kakodyle, $C_4H_{12}As_2O = Kd_2O$
Chloride of kakodyle, $C_2H_6AsCl = KdCl$.

The remarkable properties of kakodyle leave no doubt as to its being really the radical of these compounds, in the same sense in which potassium is the radical of the oxide and chloride of that metal, for kakodyle enters into direct combination with chlorine and with oxygen, its attraction for the latter being so energetic as to cause its spontaneous inflammation in the air.

The discovery of this radical, comporting itself in all respects like a metal, was of the utmost importance in its effect upon organic chemistry, affording very strong ground for belief in the existence of other quasi-metallic radicals, such as ethyle, methyle, &c., which have only recently been isolated. A similar service had been previously rendered to the science by the discovery of the compound radical *cyanogen* (CN) belonging to the electro-negative class opposed to the metals, and for a long time these two remained the only compound radicals which had been obtained in a separate form.

When kakodyle is brought gradually in contact with oxygen, it is first converted into the oxide of kakodyle ($(C_2H_6As)_2O$), and subsequently, if water be present, into *kakodylic acid* ($HC_2H_6AsO_2 = HKdO_2$), which forms prismatic crystals, unaltered by air, and destitute of poisonous character. When treated with hydrochloric or hydrosulphuric acid, it yields *terchloride* ($KdCl_3$) and *sesquisulphide of kakodyle* (Kd_2S_3).

The most poisonous member of this series is the *cyanide of kakodyle* ($C_2H_6As.CN = KdCy$), which is easily obtained in crystals by decomposing cyanide of mercury in solution with oxide of kakodyle—



$$HgCy_2 + Kd_2O = HgO + 2KdCy.$$

A very minute quantity of this substance diffused in vapour through the air has the most dangerous effect upon those inhaling it.

The following are the most important members of the kakodyle series—

Kakodyle,	$(C_2H_6As)_2 = Kd_2$
Oxide of kakodyle,	$(C_2H_6As)_2O = Kd_2O$
Sulphate of kakodyle,	$(C_2H_6As)_2O.SO_3 = Kd_2O.SO_3$
Sulphide of kakodyle,	$(C_2H_6As)_2S = Kd_2S$
Chloride of kakodyle,	$C_2H_6AsCl = KdCl$
Kakodylic acid,	$HC_2H_6AsO_2 = HKdO_2$
Kakodylate of silver,	$AgC_2H_6AsO_2 = AgKdO_2$
Sesquisulphide of kakodyle,	$(C_2H_6As)_2S_3 = Kd_2S_3$
Terchloride of kakodyle,	$C_2H_6AsCl_3 = KdCl_3$.

380. *Organo-metallic compounds.*—The only way of referring kakodyle to any known series was to regard it as an association of arsenic with two molecules of methyle (CH_3), and this supposition necessitated the existence of other compounds of a similar nature, formed, that is, by the association of an inorganic element with a quasi-metallic radical. Accordingly, within the last few years, it has been discovered that by heating the iodides of methyle, ethyle, and amyle, with zinc, compounds of those radicals with the metal can be obtained, and these compounds, like kakodyle, are distinguished by their remarkable attraction for oxygen.

Nor are arsenic and zinc the only elements with which these radicals

can be associated; boron, potassium, sodium, magnesium, aluminum, cadmium, tin, antimony, bismuth, lead, and mercury may be made to furnish similar compounds, and the principle is now fully established that the alcohol-radicals can enter into combination with metals to form compounds which are, in some cases, capable of direct union with oxygen and other electro-negative elements, for which they exhibit a greater attraction than the metals themselves.

The members of this class of *organo-metallic* bodies which have been the subjects of some of the most important researches deserve special attention.

Zinc-ethyle is prepared by the action of zinc upon iodide of ethyle—
$2C_2H_5I + Zn_2 = (C_2H_5)_2Zn + ZnI_2$.

800 grains of bright freshly granulated and thoroughly dried zinc are placed in a half-pint flask (E, fig. 293), which is connected with the carbonic acid apparatus (A),

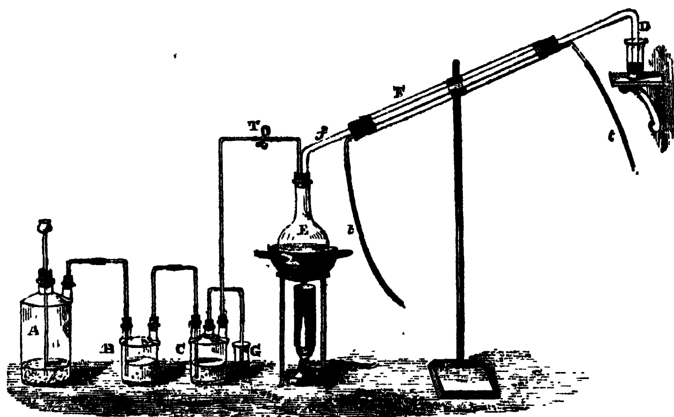


Fig. 293.—Preparation of zinc-ethyle.

from which the gas is passed through strong sulphuric acid in the bottles (B and C) where it is thoroughly dried. A second perforation in the cork of the flask (E) allows the passage of the tube *f*, which passes through the two corks in the wide tube F, and dips into a little mercury in D. A stream of cold water is kept running through the wide tube (F), being conveyed by the caoutchouc tubes *t t*. When the whole apparatus has been filled with carbonic acid, the cork of the flask (E) is removed, and 400 grains of iodide of ethyle (perfectly free from moisture) are introduced, the cork being then replaced.* The carbonic acid is again passed for a short time, and then cut off by closing the nipper-tap (T) upon a caoutchouc connector, when the gas escapes through the tube (G), which dips into mercury. A gentle heat is then applied by a water-bath to the flask (E) till the iodide of ethyle boils briskly, the vapour being condensed in the tube *f*, and running back into the flask. In about five hours the conversion is complete, and the iodide ceases to distil. The nipper-tap (T) is again opened and a slow current of carbonic acid allowed to pass; the position of the condenser (F) is reversed (fig. 294), and the tube *f* is connected, by the cork K, with the short test-tube O; the longer limb of a very narrow siphon (I) of stout tube passes through a second perforation in the cork (K), the shorter limb passing into the very short test-tube (P), the cork of which is also furnished with the short piece of moderately wide tube (L). For receiving and preserving the zinc-ethyle, a number of small tubes are prepared of the form shown in fig. 295. The long narrow neck (R) of one of these is passed down the short tube (L) to the bottom of P, the other end (N) of the tube being connected with an apparatus for passing dry car-

* The process is said to be much accelerated if about $\frac{1}{10}$th of zinc-ethyle is dissolved in the iodide of ethyle.

bonic acid. The whole of the apparatus being filled with this gas, the nipper-tap is closed, and the flask (E) heated on a sand-bath, so that the zinc-ethyle may distil over, a slow stream of carbonic acid being constantly passed into P, the excess

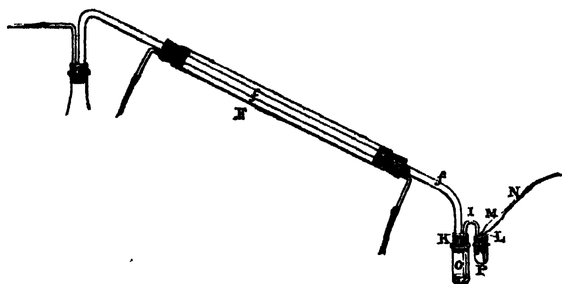


Fig. 294.—Collection of zinc-ethyle.

escaping through L. When enough zinc-ethyle has collected in the tube (O) a blow-pipe flame is applied to the narrow tube (N), which is drawn off and sealed; the syphon tube (I) is then gradually pushed down, so that its longer limb may be sufficiently immersed in the zinc-ethyle, and the nipper-tap (T, fig. 293) is opened, when the pressure of the carbonic acid forces over a part of the zinc-ethyle into the tube P. By heating the tube (M) with a spirit-lamp, so as to expel part of the carbonic acid, and allowing it to cool, it will become partly filled with zinc-ethyle, and may be withdrawn and quickly sealed by the blow-pipe. The spontaneous inflammability of the zinc-ethyle, and its easy decomposition by water, render great care necessary in its preparation. If an alloy of zinc with one-fourth its weight of sodium be employed, the conversion may be effected in an hour.

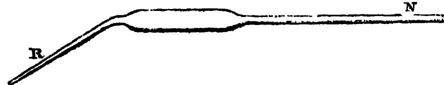
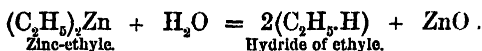


Fig. 295.

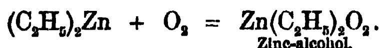
If any moisture were present in the materials employed, it would decompose a corresponding quantity of the zinc-ethyle, yielding oxide of zinc and gaseous hydride of ethyle—



$$\underset{\text{Zinc-ethyle.}}{(C_2H_5)_2Zn} + H_2O = \underset{\text{Hydride of ethyle.}}{2(C_2H_5.H)} + ZnO.$$

Zinc-ethyle is a colourless liquid of powerful odour, heavier than water (sp. gr. 1·18), and boiling at 244° F. In contact with atmospheric air, it takes fire spontaneously, burning with a dazzling greenish-blue flame, which emits white clouds of oxide of zinc. If a piece of porcelain be depressed upon the flame, a deposit of metallic zinc is formed, surrounded by a ring of oxide, which is yellow while hot, and white on cooling.

When oxygen is allowed to act very gradually upon zinc-ethyle, zinc-alcohol (or ethylate of zinc) is formed, corresponding to potassium- and sodium-alcohol (ethylates of potash and soda), which have been already described—



$$(C_2H_5)_2Zn + O_2 = \underset{\text{Zinc-alcohol.}}{Zn(C_2H_5)_2O_2}.$$

Under the gradual action of other electro-negative elements, zinc-ethyle is decomposed into compounds of zinc and ethyle with the particular element employed; $(C_2H_5)_2Zn + I_4 = 2C_2H_5I + ZnI_2$.

Zinc-methyle $(CH_3)_2Zn$ is prepared by the action of zinc upon the iodide of methyle (CH_3I), and resembles zinc-ethyle in its general character; it is, however, far more volatile and more energetic in its reactions than

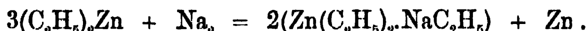
zinc-ethyle, and is decomposed with inflammation and explosion when brought in contact with water, yielding oxide of zinc and marsh-gas (hydride of methyle).



$$(CH_3)_2Zn + H_2O = 2(CH_3.H)_{\text{(Hydride of methyle.)}} + ZnO.$$

Zinc-amyle $(C_5H_{11})_2Zn$ is not so violent in its reactions; it does not inflame when exposed to air, but absorbs oxygen very rapidly.

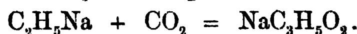
Potassium-ethyle and *sodium-ethyle* ($C_2H_5.K$ and $C_2H_5.Na$) have as yet been obtained only in combination with zinc-ethyle by heating this liquid in a sealed tube with potassium or sodium, when metallic zinc is separated, and the alkali-metal takes its place—



$$3(C_2H_5)_2Zn + Na_2 = 2(Zn(C_2H_5)_2.NaC_2H_5) + Zn.$$

The double compound of sodium-ethyle with zinc-ethyle is a crystalline solid which decomposes water with great violence, forming soda, oxide of zinc, and hydride of ethyle.* Its behaviour with carbonic acid is very interesting and important.

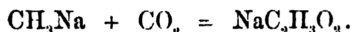
When the crystalline compound of sodium-ethyle with zinc-ethyle is introduced into a bulb-tube through which dry carbonic acid gas is passed, much heat is evolved, zinc-ethyle distils off, and a white solid is left in the bulb, which is found to consist of the propylate of soda, $NaC_3H_5O_2$ formed according to the equation—



$$C_2H_5Na + CO_2 = NaC_3H_5O_2.$$

This reaction is one of very great importance, representing the first successful attempt to produce directly one of the organic acids from carbonic acid, and indicating a general method for the formation of the other acids of the same series.

Thus, if sodium-methyle be treated in the same way, it yields acetate of soda—



$$CH_3Na + CO_2 = NaC_2H_3O_2.$$

By heating iodide of methyle in a sealed tube with a compound of arsenic and sodium, kakodyle or *arsenio-dimethyle* is obtained—



$$2\,CH_3.I) + AsNa_2 = \underset{\text{Kakodyle.}}{As(CH_3)_2} + 2NaI,$$

and thus kakodyle finds its place among the organo-metallic bodies, the existence of which it foreshadowed.

When iodide of ethyle is treated in a similar manner, *arsenio-diethyle*, $As(C_2H_5)_2$, or ethylic kakodyle, is obtained.

381. *Arsenio-trimethyle* or *trimethylarsine*, $As(CH_3)_3$, and *arsenio-triethyle* or *triethylarsine*, $As(C_2H_5)_3$, may be obtained either by acting upon the iodides of methyle and ethyle with a compound of arsenic with three atoms of sodium—



$$3(CH_3.I) + AsNa_3 = As(CH_3)_3 + 3NaI,$$

or by decomposing zinc-methyle or zinc-ethyle with terchloride of arsenic—



$$3Zn(C_2H_5)_2 + 2AsCl_3 = 2As(C_2H_5)_3 + 3ZnCl_2.$$

Arsenio-triethyle has a kakodylic odour, but does not take fire when ex-

* Strange to say when this compound of sodium-ethyle with zinc-ethyle is heated, it leaves *metallic sodium* and zinc.

posed to air, although it oxidises with great rapidity. Like kakodyle, it is capable of producing a base by combination with oxygen, which has the formula $As(C_2H_5)_3O$, and is called *arsenic triethoxide*. Similar compounds have been obtained in which the oxygen is replaced by chlorine, iodine, and sulphur.

Other arsenical compounds of ethyle and methyle have been produced, containing four equivalents of the alcohol-radical, but the oxide of tetrethyl-arsonium $[As(C_2H_5)_4]_2O$ and its congeners are really substances belonging to the ammonium family, and they will be again alluded to elsewhere.

Stibethyle, $Sb(C_2H_5)_3$, or stibiotriethyle, and stibiotrimethyle, $Sb(CH_3)_3$, are obtained by processes similar to those which furnish the corresponding compounds of arsenic, which they much resemble.

Stibethyle has a powerful odour of onions, and takes fire spontaneously in air. It combines with oxygen, chlorine, iodine, and sulphur, with great energy. So powerful is its attraction for chlorine, that it displaces hydrogen from concentrated hydrochloric acid—



$$Sb(C_2H_5)_3 + 2HCl = \underset{\text{Bichloride of stibethyle.}}{Sb(C_2H_5)_3.Cl_2} + H_2.$$

The *oxide of stibethyle* is a basic substance. The iodide of tetrethylstibonium, $Sb(C_2H_5)_4I$, belongs to the ammonium family.

Mercuric methide $Hg(CH_3)_2$ and *ethide* $Hg(C_2H_5)_2$ are formed by the action of zinc-methyle and zinc-ethyle upon bichloride of mercury—



$$Zn(C_2H_5)_2 + HgCl_2 = ZnCl_2 + Hg(C_2H_5)_2.$$

The methyle compound is the heaviest liquid (except metallic mercury) which is known; its specific gravity is 3·07, so that glass floats upon its surface.

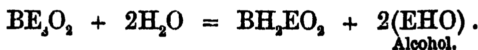
Aluminum ethide, $Al_2(C_2H_5)_6$, is obtained by decomposing mercuric ethide with aluminum, $3HgE_2 + Al_2 = Hg_3 + Al_2E_6$. It is a colourless liquid, spontaneously inflammable, and decomposed by water. The corresponding methyle compound, $Al_2(CH_3)_6$, solidifies at a little above 32° F. into a transparent crystalline mass.

Triborethyle $B(C_2H_5)_3$, has been obtained by the action of zinc-ethyle upon boracic ether—



$$\underset{\text{Boracic ether.}}{2E_3BO_3} + \underset{\text{Zinc-ethyle.}}{3ZnE_2} = \underset{\text{Triborethyle.}}{2BE_3} + \underset{\text{Ethylate of zinc.}}{3ZnE_2O_2}.$$

It distils over as a very light (sp. gr. 0·69) colourless liquid which has an irritating odour, and is insoluble in water. It inflames spontaneously in air, burning with a beautiful green flame, and explodes when brought in contact with pure oxygen. By gradual oxidation it is converted into the compound BE_3O_2, which may be distilled *in vacuo* without decomposition. When this liquid is mixed with water it is decomposed, yielding alcohol, and a volatile white crystalline body, BH_2EO_2—



$$BE_3O_2 + 2H_2O = BH_2EO_2 + 2\underset{\text{Alcohol.}}{(EHO)}.$$

This substance has an agreeable odour, and a most intensely sweet taste; it is very soluble in water, alcohol, and ether.

Boric methide, $B(CH_3)_3$, is formed by the action of a strong ethereal solution of zinc-methyle upon boracic ether—



$$\underset{\text{Boracic ether.}}{2E_3BO_3} + \underset{\text{Zinc-methyle.}}{3ZnMe_2} = \underset{\text{Boric methide.}}{2BMe_3} + \underset{\text{Ethylate of zinc.}}{3ZnE_2O_2}.$$

Boric methide is a heavy (sp. gr. 1·93) colourless gas, having an intolerably pungent tear-exciting odour, and capable of liquefaction under a pressure of three atmospheres at 50° F. When it issues very slowly into the air from a tube, it undergoes partial oxidation, and produces a lambent blue flame, invisible in daylight, and incapable of burning the fingers; but when it comes rapidly into contact with air, it burns with a bright green hot flame, remarkable for the immense quantity of large flakes of carbon which it disperses through the air, apparently because the boracic acid produced envelopes them and prevents their combustion. Boric methide combines with an equal volume of ammonia gas, producing a white, volatile compound $NH_3.BMe_3$, which is deposited in fine crystals from its ethereal solution, and may be sublimed without decomposition. Its vapour, like that of sal-ammoniac, occupies four volumes instead of two. Water absorbs very little boric methide, but alcohol dissolves it readily. Solutions of the alkalies and alkaline earths also absorb it, and potash decomposes the ammonia compound, but the combinations of boric methide with the alkalies do not crystallise, and are decomposed even by carbonic acid.

Silicium-ethyle, SiE_4, results from the decomposition of chloride of silicon with zinc-ethyle; it is not decomposed by water or by solution of potash, is lighter than water, and burns with a bright flame. Silicium-ethyle is especially interesting as the source of a new alcohol in which a part of the carbon appears to be replaced by silicon. The formula of this alcohol is said to be $SiC_8H_{20}O$, which may be represented as the (missing, see p. 512) alcohol $C_9H_{20}O$, (nonyle-alcohol), in which an atom of carbon is replaced by an atom of silicon.

Silicium-hexethyle, Si_2E_6, corresponding in composition to aluminum ethide, is also an inflammable liquid, the vapour of which has the high specific gravity 7·96.

Silicium-methyle, $Si(CH_3)_4$ is obtained by the action of chloride of silicon upon iodide of methyle in the presence of zinc. It is a liquid which burns with a luminous flame, producing white fumes of silica.

382. The following table exhibits the composition of the principal compounds of alcohol-radicals with inorganic elements which have yet been analysed, omitting some of the compound ammonias, which will be noticed hereafter:—

Compounds of alcohol-radicals with inorganic elements.	Formula.	Inorganic Type.
Sodium-ethyle, ...	NaE	$NaCl$
Magnesium-ethyle, ...	MgE_2	$MgCl_2$
Aluminum-ethyle, ...	Al_2E_6	Al_2Cl_6
Zinc-methyle, ...	$ZnMe_2$	$ZnCl_2$
Zinc-ethyle, ...	ZnE_2	$ZnCl_2$
Zinc-amyle, ...	$ZnAyl_2$	$ZnCl_2$
Stan-methyle, ...	$SnMe_2$	$SnCl_2$
Stan-ethyle, ...	SnE_2	$SnCl_2$
Sesquiethide of tin, ...	Sn_2E_6	Sn_2O_3
Diethiodide of tin, ...	$Sn_2E_4I_2$	Sn_2O_3
Stannic ethide, ...	SnE_4	$SnCl_4$

Compounds of alcohol-radicals with inorganic elements.	Formula.	Inorganic Type.
Stannic ethylomethide, . .	SnE_2Me_2*	$SnCl_4$
Stannic iodethide, ...	SnE_2I_2	$SnCl_4$
Bismuthous ethide, ...	BiE_3	$BiCl_3$
Bismuthous dichlorethide, . .	$BiECl_2$	$BiCl_3$
Plumbic ethide, ...	PbE_4	PbO_2
Mercuric ethide, ...	HgE_2	$HgCl_2$
Mercuric methide, ...	$HgMe_2$	$HgCl_2$
Stibethyle, ...	SbE_3	$SbCl_3$
Antimonic triethoxide, . .	SbE_3O	$SbCl_5$
Iodide of tetrethyl-stibonium, .	SbE_4I	$SbCl_5$
Kakodyle, ...	$AsMe_2$	As_2S_2
Oxide of kakodyle, . . .	As_2Me_4O	As_2O_3
Arsenious oxymethide, . . .	$AsMeO$	$AsCl_3$
Trimethyle-arsine, ...	$AsMe_3$	$AsCl_3$
Monomethyl arsenic acid, . .	$AsMeO_2$	$AsCl_5$
Kakodylic acid, ...	$HAsMe_2O_2$	$HAsO_3$?
Sulphokakodylic acid, . .	$(AsMe_2)_2S_3$	As_2O_5
Terchloride of kakodyle, . .	$AsMe_2Cl_3$	$AsCl_5$
Arsenic triethoxide, . . .	AsE_3O	$AsCl_5$
Oxide of tetrethylarsonium, .	$(AsE_4)_2O$	As_2O_5
Oxide of dimethyl-diethylarsonium,	$(AsMe_2E_2)_2O$	As_2O_5
Triborethyle, ...	BE_3	BCl_3
Boric methide, ...	BMe_3	BCl_3
Silicium-ethyle, ...	SiE_4	$SiCl_4$
Silicium-methyle, ...	$SiMe_4$	$SiCl_4$

These compounds are evidently formed upon the types of the inorganic combinations of the respective elements. Those elements which combine in only one proportion with oxygen or sulphur, also combine in one proportion with an alcohol-radical; whilst those which form more than one compound with oxygen and sulphur also generally form corresponding compounds with alcohol-radicals.

Thus zinc, which combines with only two atoms of chlorine or bromine, also associates itself with two of methyle, ethyle, or amyle. Aluminum also combines only in one proportion with the alcohol-radicals, but that proportion corresponds with the composition of alumina, the only oxide of aluminum.

Tin, on the other hand, forms three distinct series of compounds with the alcohol-radicals, composed according to the types of the protoxide, sesquioxide, and binoxide of tin, respectively. And it must be observed that as long as the type is adhered to, the particular radical occupying a place in the compound appears to be a matter of indifference; thus we find, in the bodies composed after the type of sesquioxide of tin (Sn_2O_3), one in which the places of the three atoms of oxygen are occupied by ethyle, and another in which only two of the places are occupied by ethyle (an electro-positive or quasi-metallic or *basylous* radical), whilst the third is filled by iodine (an electro-negative or *chlorous* radical).

* Formed by the action of zinc-methyle upon the stannic iodethide, $ZnMe_2 + SnE_2I_2 = SnE_2Me_2 + ZnI_2$.

ORGANIC ALKALOIDS—AMMONIA.

383. The attraction which the vegetable alkaloids have always possessed for the chemical inquirer is easily accounted for; composing, as they do, so very small a portion of the plants in which they are found, and yet representing, in many cases, the whole virtue and activity of such plants in their action upon the animal body, it is very natural that their composition should have been very carefully studied, with a view to explain the changes by which they are produced in the plants, and, if possible, to imitate those changes in order to obtain these valuable remedies by artificial means. In this study, however, the chemist has to contend with difficulties of no insignificant character; for even in the determination of the ultimate composition of these alkaloids, their high molecular weights and comparatively small proportion of hydrogen render the exact determination of this element a matter of great difficulty, so that even at the present time the composition of some of the less known alkaloids can hardly be said to be definitely established.

The following table includes the most important of those alkaloids which are extracted from plants:—

Alkaloid.	Source.	Formula.
Morphine	Opium	$C_{17}H_{19}NO_3$
Codeine	,,	$C_{18}H_{21}NO_3$
Narcotine	,,	$C_{22}H_{23}NO_7$
Papaverine	,,	$C_{20}H_{21}NO_4$
Quinine	Cinchona bark	$C_{20}H_{24}N_2O_2$
Cinchonine	,,	$C_{20}H_{24}N_2O$
Quinidine	,,	$C_{20}H_{24}N_2O_2$
Caffeine	Coffee	$C_8H_{10}N_4O_2$
Theine	Tea	
Theobromine	Cacao-nut	$C_7H_8N_4O_2$
Strychnine	Nux vomica	$C_{21}H_{22}N_2O_2$
Brucine	,,	$C_{23}H_{26}N_2O_4$
Nicotine	Tobacco	$C_{10}H_{14}N_2$
Solanine	Potato-shoots	
Atropine	Deadly nightshade	$C_{17}H_{23}NO_3$
Daturine	Stramonium	
Cocaine	Coca-leaves	$C_{17}H_{21}NO_4$
Hyoscyamine	Henbane	
Emetine	Ipecacuanha	
Aconitine	Aconite	
Veratrine	White hellebore	$C_{32}H_{52}N_2O_8$
Coniine	Hemlock	$C_8H_{15}N$
Piperine	Pepper	$C_{17}H_{19}NO_3$ (?)
Capsicine	Cayenne pepper	
Sparteine	Common broom	$C_{15}H_{26}N_2$
Curarine	Curara poison	$C_{10}H_{15}N$

From this table it is seen that the alkaloids invariably contain nitrogen; and though this element generally forms a comparatively small part of

the weight of the alkaloid, not exceeding 31 per cent. in theobromine, which is the richest in nitrogen, and falling as low as 3·4 per cent. in narcotine, which is the poorest, it is from this element that chemists have always started in their speculations upon the constitution of these important bodies.

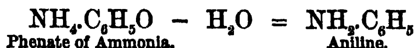
The earliest view of any importance respecting the constitution of the alkaloids was that of Berzelius, who, resting upon the constant presence of nitrogen and hydrogen in these substances, regarded them as compounds of certain neutral substances (then unknown in the separate state) with ammonia, to which they owed their alkaline characters, and this opinion was much strengthened when it was discovered that certain organic bases (though not those actually found in plants) could be produced by the direct combination of ammonia with neutral substances; thus oil of mustard (C_4H_5NS), when combined with ammonia (NH_3), yields the base *thiosinnamine* ($C_4H_8N_2S$).

To this view it was objected, that ammonia could not be detected in these organic bases, and as the doctrine of the displacement of one element by another, or by a quasi-element, gained ground, it was suggested that the organic bases might be really constituted in the same manner as ammonia itself, the place of a portion of the hydrogen being occupied by a group composed of carbon and hydrogen, or of carbon, hydrogen, and oxygen. This view of the constitution of the alkaloids, therefore, would at once propose ammonia as the type of this large class.

In the earlier attempts to refer the organic bases to ammonia as their type, it was said that just as that substance is composed of four atoms (one of nitrogen and three of hydrogen), so are the organic bases, but that these contain only two separate hydrogen-atoms, the place of the third atom of that element being occupied by a compound which discharges the functions of that third atom of hydrogen, and does not destroy the alkaline character of the original ammonia type.

To apply this view to one of the least complex of the organic bases, aniline (C_6H_7N), we might represent it as ammonia (NH_3), in which the third atom of hydrogen had been displaced by the hypothetical compound radical *phenyle* (C_6H_5) for $C_6H_7N = NH_2.C_6H_5$, *phenylamine.*

This view of the constitution of aniline was supported by the fact, that aniline may be obtained by the action of heat upon phenate of ammonia; thus—



$$\underset{\text{Phenate of Ammonia.}}{NH_4.C_6H_5O} - H_2O = \underset{\text{Aniline.}}{NH_2.C_6H_5}$$

and as the substances derived from ammoniacal salts by the loss of a molecule of water were called *amides* (being supposed to contain *amidogen*, NH_2), this theory was spoken of as the *amide-theory* of the constitution of organic bases.

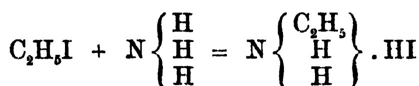
Later research has only extended this theory, having proved that ammonia is the type of at least the greater number of organic bases, and that not only one, but all three of the hydrogen-atoms, are moveable, and may be displaced by compound radicals, whilst even the nitrogen of the type also admits of replacement by other elements of the same chemical family, viz., by phosphorus, arsenic, and antimony.

A more instructive example of the elasticity of a type cannot be given.

384. *Ethylated ammonias and their derivatives.*—When iodide of ethyle (C_2H_5I) is heated in a sealed tube with an alcoholic solution of

ammonia, in the proportion of single molecules, a crystalline compound is formed, which might at first be regarded merely as a combination of the two bodies employed to produce it ($C_2H_5I.NH_3$); but when this substance is distilled with potash, it furnishes, instead of ammoniacal gas, a vapour which condenses, under the ordinary pressure in a receiver cooled by ice, to a very light colourless liquid which boils at 65°·6 F., and has a powerful ammoniacal odour. By analysis, this liquid is found to have the composition C_2H_7N, being, in fact, ammonia in which one-third of the hydrogen has been displaced by ethyle. That this is the true view of its constitution does not admit of a doubt, since it so nearly resembles ammonia in all its characters, that it might easily be mistaken for that substance. The *ethyl-ammonia* or *ethylia*, or *ethylamine*, has not only the modified odour of ammonia, but is powerfully alkaline, and combines readily with acids, forming salts, many of which may be crystallised. It is, as might be expected, more inflammable than ammonia.

The crystalline compound formed by the action of iodide of ethyle upon ammonia is the hydriodate of ethylamine—

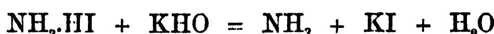


$$C_2H_5I + N\begin{cases}H\\H\\H\end{cases} = N\begin{Bmatrix}C_2H_5\\H\\H\end{Bmatrix}.HI$$

the hydrogen expelled from the ammonia having taken the place of the ethyle in the iodide, forming hydriodic acid, which remains in combination with the ethylamine.

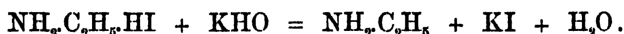
Chloride of ethyle and bromide of ethyle, when heated with ammonia, yield, respectively, the hydrochlorate and hydrobromate of ethylamine, but the iodide of ethyle is preferred for this and similar experiments, as being less volatile, and therefore, more manageable in sealed tubes.

When the hydriodate of ethylamine is distilled with potash, it behaves just as hydriodate of ammonia would do if similarly treated—



$$NH_3.HI + KHO = NH_3 + KI + H_2O$$

Hydriodate of ammonia. Ammonia.



$$NH_2.C_2H_5.HI + KHO = NH_2.C_2H_5 + KI + H_2O.$$

Hydriodate of ethylamine. Ethylamine.

Ethylamine also combines with the oxygen acids in the same manner as ammonia—



Sulphate of ammonia, ... $2NH_3.H_2O.SO_3$



Sulphate of ethylamine, . . $2(NH_2.C_2H_5).H_2O.SO_3$.

If any further proof were wanted that ethylamine is really composed after the type of ammonia, it would be afforded by the circumstance, that ethylamine may be prepared by distilling cyanic ether with caustic potash.

Cyanic ether ($C_2H_5CyO = C_2H_5CNO$) is obtained by distilling sulphovinate of potash with cyanate of potash—



$$KCyO + KC_2H_5SO_4 = C_2H_5CyO + K_2SO_4.$$

Cyanate of potash. Sulphovinate of potash. Cyanic ether.

Now, cyanic ether is simply cyanic acid, in which an atom of ethyle occupies the place of an atom of hydrogen—



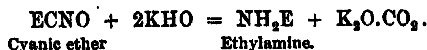
Cyanic acid, . . . HCyO
Cyanic ether, . . . ECyO.

When cyanic acid is distilled with caustic potash, it yields ammonia and carbonate of potash—



$$HCNO + 2KHO = NH_3 + K_2O.CO_2$$

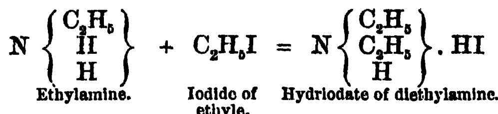
and since cyanic ether contains an atom of ethyle, in place of an atom of hydrogen, it would be expected to furnish an ammonia in which a similar displacement had been effected—



$$ECNO + 2KHO = NH_2E + K_2O.CO_2.$$

Cyanic ether — Ethylamine.

If ethylamine be again acted upon by iodide of ethyle, a second atom of hydrogen may be displaced by ethyle, and the hydriodate of *diethylamine* is obtained—

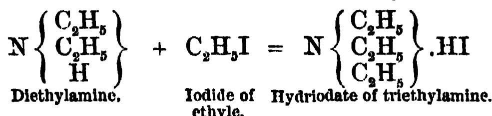


$$N\left\{\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\} + C_2H_5I = N\left\{\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}.HI$$

Ethylamine. — Iodide of ethyle. — Hydriodate of diethylamine.

and from this hydriodate the diethylamine is obtained by distillation with potash, as a colourless and inflammable liquid, strongly ammoniacal, and having a much higher boiling point than ethylamine (134°·6F.) In its chemical relations diethylamine is a decided ammonia.

In order to remove the third atom of hydrogen, it is only necessary to subject diethylamine to the action of iodide of ethyle—



$$N\left\{\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\} + C_2H_5I = N\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}.HI$$

Diethylamine. — Iodide of ethyle. — Hydriodate of triethylamine.

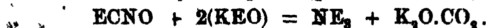
When this last hydriodate is distilled with potash, the triethylamine is obtained as a colourless liquid, presenting the strongest evidence of its relationship to ethylamine and diethylamine as well as to ammonia. It is powerfully alkaline, and boils at a higher temperature than diethylamine.*

But the action of iodide of ethyle does not stop here, for if triethylamine be again heated with it, a molecule of that base combines with a molecule of the iodide to form the compound $N(C_2H_5)_3.C_2H_5I$, which may be represented as hydriodate of triethylamine in which the place of the hydrogen in the hydriodic acid is occupied by ethyle.

But it will be remembered that the hydriodate of ammonia ($NH_3.HI$) is sometimes regarded as the iodide of a hypothetical compound metal ammonium (NH_4), and it would appear admissible to view the above compound as iodide of ammonium (NH_4I), in which the four atoms of hydrogen are displaced by ethyle; it would then be called *iodide of tetrethylammonium* (NE_4I), or iodide of tetrethylium.

Unlike the preceding compounds, the iodide of tetrethylium may be boiled with solution of potash without decomposition, but if a solution of this substance be treated with oxide of silver, iodide of silver is formed, and when the solution is filtered and evaporated *in vacuo* over sulphuric acid, it deposits needle-like crystals having the composition $N(C_2H_5)_4HO$. This substance, which is called the *hydrate of tetrethylium*, is exactly similar in properties to the hydrates of potash and soda; it is deliquescent, absorbs carbonic acid eagerly from the air, is exceedingly alkaline and caustic, expels ammonia from its salts, forms soap with the fats, and behaves in every respect like the hydrate of a fixed alkali. Its taste is very bitter as well as alkaline.

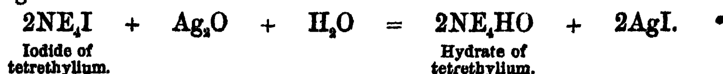
* Just as ethylamine is obtained by the action of hydrate of potash upon cyanic ether, so triethylamine is formed when ethylate of potash (potassium-alcohol) acts upon cyanic ether—



$$ECNO + 2(KEO) = NE_3 + K_2O.CO_2.$$

It is obviously not an ammonia, but is composed after the type of caustic potash (KHO), and contains, in place of the potassium, the hypothetical radical tetrethylium, $N(C_4H_5)_4$, or ammonium (NH_4) in which the four atoms of hydrogen have been displaced by ethyle.

The action of oxide of silver upon the iodide of tetrethylium is now intelligible—



$$2NE_4I + Ag_2O + H_2O = 2NE_4HO + 2AgI.$$

Iodide of tetrethylium. Hydrate of tetrethylium.

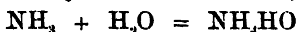
The new alkali is easily decomposed; even at a temperature below the boiling point of water, it is resolved into triethylamine, olefiant gas, and water—



$$N(C_2H_5)_4HO = N(C_2H_5)_3 + C_2H_4 + H_2O.$$

Triethylamine.

It will be remembered that the solution of ammonia in water may be regarded as containing the hydrate of ammonium, for—



$$NH_3 + H_2O = NH_4HO$$

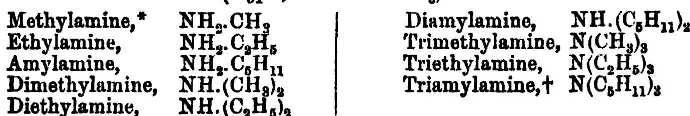
which latter would be the true type of the hydrate of tetrethylium; but so great is the want of stability in this case, that all attempts to isolate the hydrate of ammonium have resulted in the production of ammonia and water.

Like potash, the oxide of tetrethylium is capable of forming salts with the oxygen-acids without the intervention of a molecule of water, thus—



Sulphate of potash, . . .	$K_2O.SO_3$
Sulphate of oxide of tetrethylium,	$(NE_4)_2O.SO_3$.

It would naturally be expected that by the action of the iodides of other alcohol radicals upon ammonia, compounds should be obtained corresponding to those belonging to the ethyle series; thus we have—

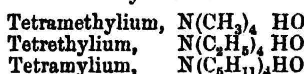


(*Type;* ammonia NH_3).

Methylamine,*	$NH_2.CH_3$	Diamylamine,	$NH.(C_5H_{11})_2$
Ethylamine,	$NH_2.C_2H_5$	Trimethylamine,	$N(CH_3)_3$
Amylamine,	$NH_2.C_5H_{11}$	Triethylamine,	$N(C_2H_5)_3$
Dimethylamine,	$NH.(CH_3)_2$	Triamylamine,†	$N(C_5H_{11})_3$
Diethylamine,	$NH.(C_2H_5)_2$		

(*Type;* imaginary hydrate of ammonium, NH_4HO.)

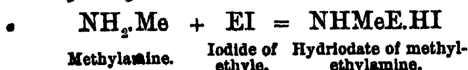
Hydrate of—



Tetramethylium,	$N(CH_3)_4\,HO$
Tetrethylium,	$N(C_2H_5)_4\,HO$
Tetramylium,	$N(C_5H_{11})_4HO$

But even here, the elasticity of the types and the replacing power of the alcohol-radicals are not exhausted.

If methylamine ($NH_2.Me$) be acted upon by iodide of ethyle, the hydriodate of *methyl-ethylamine* is formed—



$$NH_2.Me + EI = NHMeE.HI$$

Methylamine. Iodide of ethyle. Hydriodate of methyl-ethylamine.

* Methylamine, which is a gas at the ordinary temperature, is far more soluble in water than any other gas; water dissolves 1150 volumes of methylamine, the solution exactly resembling that of ammonia.

† Even the hypothetical hydrocarbon cetyle ($C_{16}H_{33}$), the radical of ethal, has been substituted for the nitrogen in ammonia. The base *tricetylamine*, $N(C_{16}H_{33})_3$, which is thus formed, contains only 2 per cent. of nitrogen.

and by distilling this with potash, the methyl-ethylamine, much resembling the other ammonia bases, is obtained.

Again, on subjecting this base to the action of iodide of amyle, and distilling the product with potash, a new ammonia base is procured, in which all three atoms of hydrogen are replaced by different radicals; this base is called methyl-ethyl-amylamine, and its composition is represented by the formula $N(CH_3)(C_2H_5)(C_5H_{11}) = NMeEAyl$.

If we had started with aniline (phenylamine, $NH_2.C_6H_5$) in the above experiment, treatment with iodide of methyle would have furnished methyl-aniline or methyl-phenylamine, $NH.C_6H_5.CH_3$; and by treating this with iodide of ethyle, we should obtain ethyl-methyl-phenylamine, $NC_6H_5.CH_3.C_2H_5$; the action of iodide of amyle upon this last ammonia would give the iodide of methyl ethyl-amylo-phenylium, and on decomposing this with oxide of silver there would be obtained the hydrate of methyl-ethyl-amylo-phenyl-ammonium—



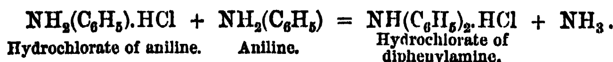
$$N(CH_3)(C_2H_5)(C_5H_{11})(C_6H_5)HO$$

a base formed upon the hypothetical type of hydrate of ammonium, in which each of the four atoms of hydrogen is replaced by a different radical.

This complex substance affords an excellent example of the difference between an empirical and a rational formula; its empirical formula, $C_{14}H_{25}NO$, which simply shows the result of its ultimate analysis, teaches nothing with respect to its constitution, which is at once clear when the rational formula as above written is placed before us.

Phenylamine, $NH_2(C_6H_5)$, is found among the products of the destructive distillation of rosaniline (p. 452), whilst ethyl-rosaniline (aniline-violet) yields *ethyl-phenylamine* or *ethyl-aniline*, $NH(C_6H_5)(C_2H_5)$, and phenyl-rosaniline (*aniline blue*) yields *di-phenylamine* or *phenyl-aniline*, $NH(C_6H_5)_2$.

Diphenylamine has also been obtained by digesting hydrochlorate of aniline with free aniline at a high temperature, when hydrochlorate of diphenylamine is obtained, which is decomposed by a large excess of warm water, the diphenylamine rising to the surface as an oil which solidifies on cooling. The change may be expressed by the following equation :—



$$\underset{\text{Hydrochlorate of aniline.}}{NH_2(C_6H_5).HCl} + \underset{\text{Aniline.}}{NH_2(C_6H_5)} = \underset{\text{Hydrochlorate of diphenylamine.}}{NH(C_6H_5)_2.HCl} + NH_3.$$

Ditoluylamine, $NH(C_7H_7)_2$, may be procured in a similar way by digesting hydrochlorate of toluidine with toluidine.

Phenyl-toluylamine, $NH(C_6H_5)(C_7H_7)$, is formed by the action of aniline on hydrochlorate of toluidine, or by that of toluidine on hydrochlorate of aniline.

Under the action of nitric acid, di-phenylamine gives rise to di-nitro-diphenylamine, $NH[C_6H_4(NO_2)]_2$, in which the same type is preserved, though nitric peroxide (NO_2) is substituted for one-fifth of the hydrogen in the phenyle.

When treated with chloride of benzoyle ($C_7H_5O.Cl$), diphenylamine yields diphenyl-benzoylamine, $N(C_6H_5)_2(C_7H_5O)$.

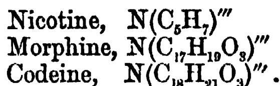
It will be observed that certain of these bases derived from the alcohols have the same empirical formulæ as those derived from coal-tar and other sources, with which, however, they are by no means identical. Thus, toluidine (C_7H_9N) has the same composition as methyl-aniline ($NH.C_6H_5.CH_3$); but the former is a crystalline solid, and the latter an oily liquid. Again, when iodide of ethyle acts upon toluidine, an atom of hydrogen is displaced by ethyle, and *ethylo-toluidine* is obtained. The *composition* of this base, $C_7H_8(C_2H_5)N$, is the same as that of methyl-ethyl-aniline, $N(CH_3)(C_2H_5)(C_6H_5)$, and as that of cumidine ($C_9H_{13}N$); but in their

chemical properties these bodies exhibit such a difference as would be expected from the difference in their *constitution.*

385. *Investigation of the constitution of the alkaloids.*—It will be evident that the principles developed in the experiments just described may be applied in investigating the constitution of the bases extracted from plants. Let it be supposed that ethylamine (C_2H_7N) was a vegetable alkali of unknown constitution; when it was found that by the action of iodide of ethyle two out of the seven atoms of hydrogen could be displaced, it would be at once inferred that these two atoms occupied a very different position from the other five, and that the constitution of the compound would be more properly expressed by writing the formula $C_2H_5.H_2N$. On applying the same principle to the examination of the natural alkaloid coniine ($C_8H_{15}N$), it was found possible, by the action of iodide of methyle, to remove only one atom of the hydrogen, so that the formula $C_8H_{14}.HN$ would more correctly represent the constitution of coniine, which might be then regarded as ammonia in which two atoms of the hydrogen have been displaced by the group C_8H_{14}, or in which each of these atoms has been displaced by the group C_4H_7.

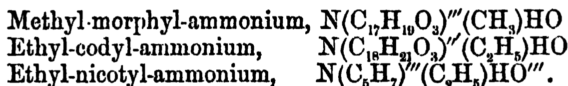
If we were acquainted with an iodide of this group, we have every reason to expect that its action upon ammonia would lead us to the artificial formation of coniine.*

Nicotine, morphine, and codeine will not part with any of their hydrogen under the action of iodide of ethyle, and must therefore be placed upon the same footing as triethylamine, $N(C_2H_5)_3$, in which all three atoms of hydrogen are already replaced. Upon this view they would be represented thus—



Nicotine, $N(C_5H_7)'''$
Morphine, $N(C_{17}H_{19}O_3)'''$
Codeine, $N(C_{18}H_{21}O_3)'''$.

The mark (''') signifying that the groups are *triatomic*, or have the same replacing value as three atoms of hydrogen. When these bases are acted upon by the iodides of alcohol-radicals, there are formed, as would be expected, iodides upon the type NH_4I, from which may be obtained fixed alkalies resembling the hydrate of tetrethylium. Thus we have the hydrates



Methyl-morphyl-ammonium, $N(C_{17}H_{19}O_3)'''(CH_3)HO$
Ethyl-codyl-ammonium, $N(C_{18}H_{21}O_3)'''(C_2H_5)HO$
Ethyl-nicotyl-ammonium, $N(C_5H_7)'''(C_2H_5)HO'''$.

386. *Poly-ammonias.*—In speculating upon the constitution of the vegetable bases, it must not be forgotten that some of them contain two atoms of nitrogen; this is the case, for example, with cinchonine ($C_{20}H_{24}N_2O$), quinine ($C_{20}H_{24}N_2O_2$), and strychnine ($C_{21}H_{22}N_2O_2$). If the whole of the nitrogen in these bases be due to the ammonia type, they must be composed after the type of a double atom of ammonia, N_2H_6. In the case of strychnine, it is found that the action of iodide of ethyle fails to remove any portion of the hydrogen, so that if the base be really composed after the ammonia type, it must be represented by two atoms of ammonia (N_2H_6), in which the whole of the hydrogen has been displaced

* The group C_4H_7 is often assumed as the radical of butyric acid ($C_4H_8O_2$), and it is at least a curious coincidence, that when acted upon by nitric acid, coniine actually yields butyric acid.

by the group $(C_{21}H_{22}O_2)$, when its formula would be $N_2(C_{21}H_{22}O_2)^{vi}$, the replacing group in this case being *hexatomic*, or equivalent to six atoms of hydrogen. That it is by no means necessary for each atom of hydrogen to be displaced by a single group or radical, is seen in a great many organic compounds; thus, in chloroform $(CH)Cl_3$, we have the triatomic group CH (commonly called formyle) occupying the position of three atoms of hydrogen which would be required to combine with the three atoms of chlorine; again, in Dutch liquid, $(C_2H_4)Cl_2$, we have the diatomic group C_2H_4 (ethylene) occupying the place of two atoms of hydrogen.

If the view above explained with respect to the constitution of some of the natural alkaloids be correct, it ought to be possible to form artificially a base in which two or three atoms of hydrogen have been displaced by means of a diatomic or triatomic radical.

387. *Diamines.*—When olefiant gas or ethylene, C_2H_4, is brought in contact with bromine, the compound $C_2H_4Br_2$, corresponding to Dutch liquid $(C_2H_4Cl_2)$, is obtained, and from the action of ammonia upon this *bibromide of ethylene*, there is derived a new alkaline base, having the composition $N_2H_4(C_2H_4)''$, or two molecules of ammonia (N_2H_6), in which the diatomic ethylene replaces two atoms of hydrogen. Such bases, formed upon the double ammonia type, are called *diamines*, whilst those which correspond to a single molecule of ammonia are called *monamines*. The base above mentioned is named *ethylene-diamine*. The diamines, like the double atom of ammonia from which they are derived, are capable of combining with two molecules of hydrochloric or any similar acid, which is implied by stating that they are *diacid*.

When Dutch liquid (*bichloride of ethylene*, $(C_2H_4)''Cl_2$), is heated to 300° F. with strong ammonia in a sealed tube, an action takes place corresponding to that of a double molecule of hydrochloric acid (H_2Cl_2) upon a double molecule of ammonia (N_2H_6), which would give rise to a double molecule of hydrochlorate of ammonia $(N_2H_6.H_2Cl_2)$; in the product of the action of Dutch liquid upon ammonia $(N_2H_4(C_2H_4)_2''Cl_2)$, the places of four atoms of hydrogen are occupied by two molecules of the diatomic group (C_2H_4). But here the correspondence ceases, for whilst the hydrochlorate of ammonia, when decomposed with oxide of silver, would yield ammonia and chloride of silver, the new compound, when thus treated, yields a fixed alkaline base, resembling caustic potash, and having the composition $N_2H_4(C_2H_4)_2''.H_2O_2$, which represents a double molecule of the hypothetical hydrate of ammonium $2(NH_4HO)$, in which four atoms of hydrogen have been displaced by two molecules of the diatomic ethylene. The name *hydrate of diethylene-diammonium* expresses the composition of this substance, which is remarkable for its stability, a temperature above 300° F. being required to effect its decomposition, when it furnishes a volatile alkali, having the composition $N_2H_2(C_2H_4)_2''$, and called diethylene-diamine, being evidently formed from a double molecule of ammonia, in which four atoms of hydrogen are replaced by two of the diatomic ethylene. Its production may be explained by the equation—



$$N_2H_4(C_2H_4)_2''H_2O_2 = N_2H_2(C_2H_4)_2'' + 2H_2O.$$

By acting upon the new ammonia with iodide of ethyle (C_2H_5I), the two atoms of hydrogen may be displaced by ethyle, yielding *diethyl-diethylene-diamine*, $N_2(C_2H_5)_2(C_2H_4)_2''$, or a double molecule of ammonia (N_2H_6), in which H_2 are replaced by two of ethyle, and H_4 by two of ethylene.

By treating phenylamine (aniline), $NH_2(C_6H_5)$, with bichloride of ethylene (Dutch liquid), the *diphenyl-diethylene-diamine*, $N_2(C_6H_5)_2(C_2H_4)_2''$, is obtained, which represents a double molecule of ammonia (N_2H_6), in which H_2 are replaced by two of phenyle, and H_4 by two of ethylene. By the action of chloroform upon aniline, *formyl-diphenyl-diamine*, $N_2(CH)'''(C_6H_5)_2H$, has been obtained, in which H_3 are replaced by the triatomic formyle (CH), and H_2 by phenyle.

It has been seen that phenylamine is produced by the deoxidising action of ferrous acetate upon nitrobenzole $(C_6H_5.NO_2)$. When di-nitrobenzole is treated in a similar way, *phenylene-diamine*, $N_2H_4(C_6H_4)''$, is obtained, which is evidently derived from a

double molecule of ammonia, in which H_2 are replaced by the diatomic group *phenylene* (C_6H_4), which bears the same relation to phenyle (C_6H_5) as ethylene (C_2H_4) bears to ethyle (C_2H_5). By treating di-nitrotoluole and di-nitrocumole with ferrous acetate, *tolylene-diamine* and *cumylene-diamine* are obtained, which are diammonias, in which H_2 are replaced by the diatomic radicals *tolylene* $(C_7H_6)''$ and *cumylene* $(C_9H_{10})''$. These three diamines are called the *aromatic diamines*, since the diatomic groups phenylene, tolylene, and cumylene are closely connected, through benzole (C_6H_6), toluole (C_7H_8), and cumole (C_9H_{12}), with the *aromatic acids*, benzoic $(C_7H_6O_2)$, toluic $(C_8H_8O_2)$, and cuminic $(C_{10}H_{12}O_2)$.

Paraniline $(C_{12}H_{14}N_2)$ is obtained as a secondary product in the manufacture of aniline, with which it is polymeric. Its properties are very different from those of aniline, for it is solid at the ordinary temperature, forming silky needles which melt when heated, and boil beyond the range of the thermometer, distilling unchanged. It combines with acids, forming beautiful crystalline salts, the study of which proves it to be a diamine.

388. *Triamines.*—The triamines are formed upon the type of a treble molecule of ammonia (N_3H_9), in which the hydrogen is replaced either entirely or in part by other radicals. Thus, *diethylene-triamine*, $N_3H_5(C_2H_4)_2''$, and *triethylene-triamine*, $N_3H_3(C_2H_4)_3''$, are obtained by the action of bi-bromide of ethylene $(C_2H_4Br_2)$ upon ammonia. They are powerfully alkaline liquids, which are capable of absorbing carbonic acid from the air. The triamines are generally capable of forming three classes of salts, the *monacid*, *diacid*, and *triacid* salts, containing respectively one, two, and three equivalents of acid.

Di-ethylene-di-ethyl-triamine, $N_3H_3(C_2H_4)_2''(C_2H_5)_2$, is produced by the joint action of ethylamine and ammonia upon bibromide of ethylene—



$$2[(C_2H_4)''Br_2] + 3NH_2(C_2H_5) + NH_3 = N_3H_3(C_2H_4)_2''(C_2H_5)_2.3HBr + NH_2(C_2H_5).HBr.$$

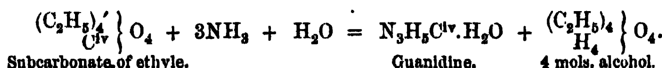
It forms splendidly crystallised salts, and is evidently derived from three molecules of ammonia (N_3H_9), by the substitution of two molecules of ethylene $(C_2H_4)_2''$ for H_4, and of ethyle $(C_2H_5)_2$ for H_2.

Carbotriamine (guanidine), $N_3H_5C^{iv}$, is a treble molecule of ammonia, in which four atoms of hydrogen are replaced by one atom of tetratomic carbon. It is formed by heating ammonia with subcarbonate (orthocarbonate) of ethyle in a sealed tube to about 300° F.



$$2(C_2H_5)_2O.CO_2 + 3NH_3 + H_2O = N_3H_5C.H_2O + 4(C_2H_5HO).$$

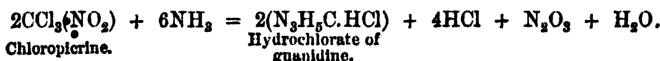
The change is more clearly explained by representing the subcarbonate of ethyle as formed upon the type of four molecules of water (H_8O_4) in which H_4 are replaced by $(C_2H_5)_4$, and the remaining H_4 by C^{iv}.



$$\left.\begin{matrix}(C_2H_5)_4' \\ C^{iv}\end{matrix}\right\} O_4 + 3NH_3 + H_2O = N_3H_5C^{iv}.H_2O + \left.\begin{matrix}(C_2H_5)_4 \\ H_4\end{matrix}\right\} O_4.$$

Subcarbonate of ethyle. Guanidine. 4 mols. alcohol.

Guanidine may also be obtained by heating chloropicrine in a sealed tube, with an alcoholic solution of ammonia, to 212° F., when the following reaction ensues—



$$2CCl_3(NO_2) + 6NH_3 = 2(N_3H_5C.HCl) + 4HCl + N_2O_3 + H_2O.$$

Chloropicrine. Hydrochlorate of guanidine.

It will be remembered that the subcarbonate of ethyle itself is obtained by the action of sodium upon an alcoholic solution of chloropicrine (p. 516).

Melaniline, $C_{13}H_{13}N_3$, a crystalline base, produced by the action of chloride of cyanogen upon aniline, may be regarded as *diphenyl-guanidine*, $N_3H_3(C_6H_5)_2C$, or guanidine in which two of phenyle have replaced two of hydrogen.

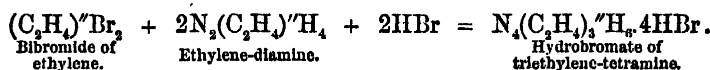
The beautiful aniline dyes appear to be salts of certain triamines formed by the replacement of the hydrogen in a treble molecule of ammonia by hydrocarbon radicals.

According to Hofmann, rosaniline, the base of the aniline red produced by the action of oxidising agents upon aniline containing toluidine, is possibly *phenylene-ditolylene-triamine*, $N_3(C_6H_4)''(C_7H_6)_2''H_3.H_2O$, the phenylene being derived from the

aniline, $NH_2(C_6H_5)$, and the tolylene from the toluidine, $NH_2(C_7H_7)$. Aniline blue, formed by the action of aniline upon aniline red, would be *phenylene-ditolylene-triphenyl-triamine*, $N_3(C_6H_4)''(C_7H_6)_2''(C_6H_5)_3.H_2O$, having been formed from rosaniline by the substitution of three of phenyle for H_3. Aniline violet, the result of the action of iodide of ethyle upon rosaniline, would be *phenylene-ditolylene triethyl-triamine*, $N_3(C_6H_4)''(C_7H_6)_2''(C_2H_5)_3.H_2O$, or rosaniline containing three of ethyle in place of H_3.

The *trichloride of diethylene-triammonium*, $N_3(C_2H_4)_2''H_8.Cl_3$, has also been obtained.

389. *Tetramines* are formed upon the type of four molecules of ammonia, and therefore contain four atoms of nitrogen, and are able to combine with four atoms of a hydrogen acid. Thus, if bibromide of ethylene be allowed to act upon ethylene-diamine in the presence of hydrobromic acid, the hydrobromate of triethylene-tetramine is obtained—



$$\underset{\text{Bibromide of ethylene.}}{(C_2H_4)''Br_2} + \underset{\text{Ethylene-diamine.}}{2N_2(C_2H_4)''H_4} + 2HBr = \underset{\text{Hydrobromate of triethylene-tetramine.}}{N_4(C_2H_4)_3''H_6.4HBr.}$$

and if this be decomposed with oxide of silver, a strongly alkaline solution is obtained, which contains triethylene-tetramine, $N_4(C_2H_4)_3''H_6$, or a quadruple molecule of ammonia (N_4H_{12}), in which half the hydrogen is replaced by three of diatomic ethylene.

By acting on $C_2H_4Br_2$ with ethylamine, a salt is obtained, having the composition $N_4(C_2H_4)_5''(C_2H_5)_4H_2.Br_4$, representing four molecules of bromide of ammonium $(N_4H_{16}Br_4)$, in which H_{10} are replaced by $5(C_2H_4)''$, and H_4 by $(C_2H_5)_4$. From this bromide a strongly alkaline base, the hydrate of *pentethylene-tetrethyl-tetr-ammonium* $[N_4(C_2H_4)_5''(C_2H_5)_4H_2]H_4O_4$ is obtained, which is formed upon the type of four molecules of the imaginary hydrate of ammonium (NH_4HO).

The action of iodide of ethyle (C_2H_5I) upon this base replaces each of the remaining atoms of hydrogen by ethyle, yielding $[N_4(C_2H_4)_5''(C_2H_5)_5H]H_4O_4$ and $[N_4(C_2H_4)_5''(C_2H_5)_6]H_4O_4$.

When diethylamine $(NH(C_2H_5)_2)$ acts on bibromide of ethylene, the bromide of *tri-ethylene-octethyl-tetrammonium*, $N_4(C_2H_4)_3''(C_2H_5)_8H_2.Br_4$, is obtained, which also furnishes a powerfully alkaline base $[N_4(C_2H_4)_3''(C_2H_5)_8H_2]H_4O_4$.

390. We are not entirely dependent upon purely artificial processes for the ammonia bases containing alcohol-radicals. Many processes of putrefaction furnish certain of these bases which had hitherto been overlooked in consequence of their resemblance to ammonia. Thus, putrefying flour yields ethylamine, trimethylamine, and amylamine; trimethylamine is also found in the roe of herrings, as also in putrefied urine and in the *chenopodium vulvaria;* it may also be obtained by distilling ergot of rye with potash. Methylamine, ethylamine, *propylamine* $(NH_2.C_3H_7)$, *butylamine* $(NH_2.C_4H_9)$, or *petinine*, and amylamine, are found among the products of the destructive distillation of bones.

391. *Ammonias and ammonium bases containing phosphorus, arsenic, and antimony.*—It might be expected that the ammonia type was not susceptible of any further modifications, but it has been found that even the nitrogen of that type may be represented by other elements which are chemically related to it.

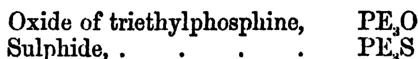
Antimony, arsenic, and phosphorus, it will be remembered, all form compounds with three atoms of hydrogen, SbH_3, AsH_3, and PH_3, which may be regarded as formed upon the ammonia type. Neither of these substances, however, possesses any alkaline character, the last alone being capable of combining with certain acids (hydrobromic and hydriodic).

Mention has already been made of the circumstance that compounds corresponding to antimonietted, arsenietted, and phosphuretted hydrogen

may be obtained, in which the place of the hydrogen is occupied by certain alcohol-radicals; but in these cases the hydrogen does not admit of partial replacement, only those compounds which correspond to triethylamine and trimethylamine having been obtained.

Triethylstibine, $Sb(C_2H_5)_3$, and *triethylarsine*, $As(C_2H_5)_3$, have already been noticed amongst another class of bodies to which they seem properly to belong, since they are not capable of forming salts corresponding to those of ammonia (see p. 528).

With *triethylphosphine*, however, the case is different; this substance, $P(C_2H_5)_3$, is a true ammonia, capable of forming salts with the acids, like ethylamine, although exhibiting, unlike that body, a very powerful tendency to combine directly with an atom of oxygen or sulphur, to form compounds resembling those of the arsenic and antimony series (see p. 528), and formed upon the type of phosphoric chloride (PCl_5). Thus we have—



Oxide of triethylphosphine,	PE_3O
Sulphide, ...	PE_3S

and the corresponding compounds containing methyle.

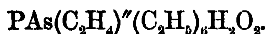
Triethylphosphine is obtained by the action of terchloride of phosphorus upon zinc-ethyle, $2PCl_3 + 3ZnE_2 = 2PE_3 + 3ZnCl_2$. It is a volatile liquid of a very peculiar powerful odour, the vapour of which, when mixed with oxygen, explodes with great violence at a temperature far below 212°.

By acting upon triethylstibine, or stibio-triethyle, with iodide of ethyle, an iodide is obtained which, when decomposed by oxide of silver, yields the hydrate of tetrethylstibonium (SbE_4HO), formed after the type of hydrate of ammonium (NH_4HO).

In a similar manner there are obtained the hydrates of *tetrethylarsonium* (AsE_4HO) and tetrethylphosphonium (PE_4HO), and their corresponding methyle compounds.

These substances are precisely similar in properties to the hydrate of tetrethylium, being powerfully caustic alkalies bearing a close resemblance to caustic potash.

A very remarkable base has also been obtained, composed after the type of a double molecule of the imaginary hydrate of ammonium ($N_2H_8H_2O_2$), in which one atom of nitrogen has been replaced by phosphorus, and the other by arsenic, whilst, of the hydrogen, two atoms are replaced by the diatomic radical ethylene $(C_2H_4)''$, and the remainder by ethyle. This base has been styled the hydrate of ethylene-hexethyle-diphospharsonium, and its formula is—



$$PAs(C_2H_4)''(C_2H_5)_6H_2O_2.$$

This base combines with two molecules of acids to form salts, and behaves in every respect as a double molecule of caustic potash would do.

By acting upon triethylphosphine with *chloroform* ($CHCl_3$), containing the triatomic radical formyle $(CH)'''$, a chloride has been obtained which is composed upon the type of three molecules of chloride of ammonium ($3NH_4Cl = N_3H_{12}Cl_3$), in which one-fourth of the hydrogen is replaced by formyle and the rest by ethyle; the composition of this chloride is therefore ($P_3(CH)'''(C_2H_5)_9Cl_3$); from this compound various salts have been obtained containing the corresponding oxide, combined with three molecules of the acids, but the hydrate itself has not been obtained.

$$3P(C_2H_5)_3 + (CH)'''Cl_3 = P_3(CH)'''(C_2H_5)_9Cl_3.$$

Triethylphosphine. Chloroform. Trichloride of formyl-nonethyl-triphosphonium.

392. The insight into the constitution of the bases derived from ammonia, which has been acquired in the researches detailed above, has induced chemists to endeavour to apply the same principles to certain inorganic bases derived from ammonia by the action of metallic salts.

Thus, by the action of (proto) chloride of platinum upon ammonia (see p. 392), a compound is obtained which may be regarded as simply $PtCl_2(NH_3)_2$, but when this is treated with oxide of silver, the Cl is removed in the form of chloride of silver, and a caustic alkaline base is separated, which has the formula $PtO.(NH_3)_2$, or rather, viewed upon the type of oxide of ammonium, N_2H_6PtO oxide of platammonium.

By employing ethylamine instead of ammonia there would be obtained $N_2H_4E_2PtO$ oxide of ethyloplatammonium.

When the compound $PtCl_2(NH_3)_2$ (or rather $N_2H_6Pt.Cl_2$ chloride of platammonium) is again treated with ammonia, it yields $N_2H_6Pt.Cl_2(NH_3)_2$, and when this is decomposed with oxide of silver, another caustic alkali is obtained, having the composition $N_2H_6Pt(NH_3)_2H_2O_2$ which may be regarded as $N_2H_4Pt(NH_4)_2H_2O_2$ the hydrate of platammon-ammonium (hydrate of diplatosamine); it would then become a double molecule of hydrate of ammonium (NH_4HO), in which two atoms of hydrogen are replaced by platinum and two by ammonium.

Very remarkable and beautiful crystalline compounds have also been obtained, which are formed after the type of chloride of platammonium, but contain either phosphorus, antimony, or arsenic, in place of nitrogen, and ethyle in place of hydrogen; these are—

Chloride of *plato-triethyl-diphosphonium*, .	$P_2Pt(C_2H_5)_6.Cl_2$
,, ,, *arsonium*, . .	$As_2Pt(C_2H_5)_6.Cl_2$
,, ,, *stibonium*, . .	$Sb_2Pt(C_2H_5)_6.Cl_2$

Corresponding salts have also been obtained containing gold in the place of platinum, and forming beautiful *colourless* crystals.

In some bases, chlorine, bromine, and even nitric peroxide (NO_2) have been introduced in the place of hydrogen into the alcohol-radical, but in all these cases the basic energy is diminished by such substitution, and in some altogether destroyed.

Thus, in the aniline (phenylamine) series, we have—

Chloraniline, . . .	$NH_2(C_6H_4Cl)$, weak base.
Dichloraniline, . . .	$NH_2(C_6H_3Cl_2)$, weaker base.
Trichloraniline, . . .	$NH_2(C_6H_2Cl_3)$, neutral.
Nitraniline, . . .	$NH_2[C_6H_4(NO_2)]$, weak base.
Dinitraniline, . . .	$NH_2[C_6H_3(NO_2)_2]$, neutral.

393. *Amides.*—When oxalate of ammonia $(NH_4)_2C_2O_4$ is subjected to distillation, a white, crystalline sparingly soluble substance is obtained, which has been named *oxamide*, and is represented by the formula $(NH_2)_2C_2O_2$. This substance is derived from the ammonia-salt by the loss of 2 molecules of water—

$$(NH_4)_2C_2O_4 - 2H_2O = (NH_2)_2C_2O_2$$

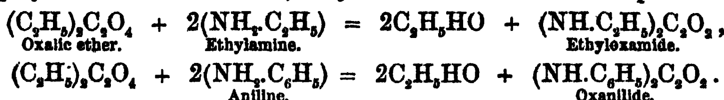
and its close relationship to oxalate of ammonia is shown by the circumstance that it is reconverted into that salt, if heated with water in a sealed tube to 436° F., or by simply boiling it with water to which a little acid or alkali has been added.

Oxamide is more readily prepared by decomposing oxalic ether with ammonia, when it is obtained as a white crystalline precipitate—

$$(C_2H_5)_2C_2O_4 + 2NH_3 = 2C_2H_5HO + (NH_2)_2C_2O_2.$$

Oxalic ether. Alcohol. Oxamide.

If one of the compound ammonias, such as ethylamine and aniline, be employed instead of ammonia, *ethlyoxamide* and *oxanilide* are produced—



$$\underset{\text{Oxalic ether.}}{(C_2H_5)_2C_2O_4} + \underset{\text{Ethylamine.}}{2(NH_2.C_2H_5)} = 2C_2H_5HO + \underset{\text{Ethyloxamide.}}{(NH.C_2H_5)_2C_2O_2},$$

$$(C_2H_5)_2C_2O_4 + \underset{\text{Aniline.}}{2(NH_2.C_6H_5)} = 2C_2H_5HO + \underset{\text{Oxanilide.}}{(NH.C_6H_5)_2C_2O_2}.$$

Oxamide is the representative of a large class of bodies, known as the *amides*, which may be defined as substances capable of being converted, by the assimilation of the elements of water, into the ammonia-salts from which they are derived.

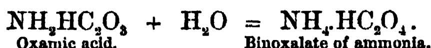
Some other interesting members of this class are here enumerated, together with the corresponding ammonia-salts—

Formamide, . . .	$NH_2.CHO$	Formiate of ammonia,	$(NH_4).CHO_2$
Acetamide, . . .	$NH_2.C_2H_3O$	Acetate, ...	$(NH_4).C_2H_3O_2$
Butyramide, . . .	$NH_2.C_4H_7O$	Butyrate, ...	$(NH_4).C_4H_7O_2$
Benzamide, . . .	$NH_2.C_7H_5O$	Benzoate, ...	$(NH_4).C_7H_5O_2$

It is evident that these amides may be regarded as derived from ammonia by the substitution of a compound group for one of the three atoms of hydrogen.

When binoxalate of ammonia ($NH_4HC_2O_4$) is distilled, at a moderate heat, a solid acid substance is left in the retort, which is known as *oxamic acid*, $NH_2.HC_2O_3$, and forms soluble crystallisable salts with lime and baryta, both which bases yield insoluble salts with oxalic acid.

When the solution of oxamic acid in water is boiled, it is reconverted into the binoxalate of ammonia—

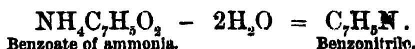


$$\underset{\text{Oxamic acid.}}{NH_2HC_2O_3} + H_2O = \underset{\text{Binoxalate of ammonia.}}{NH_4.HC_2O_4}.$$

Oxamic acid is the representative of a limited class of acids formed in a similar manner.

394. *Nitriles.*—When oxalate of ammonia is mixed with anhydrous phosphoric acid and distilled, it loses 4 molecules of water, leaving cyanogen $(NH_4)_2C_2O_4 - 4H_2O = 2CN$.

In a similar manner, benzoate of ammonia yields *benzonitrile*—



$$\underset{\text{Benzoate of ammonia.}}{NH_4C_7H_5O_2} - 2H_2O = \underset{\text{Benzonitrile.}}{C_7H_5N}.$$

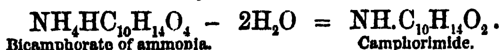
The new compound is an oil which has a powerful odour of bitter almonds, and is reconverted into benzoate of ammonia by boiling with dilute acids or alkalies.

The term *nitrile* is applied to all similar substances which are derived from ammoniacal salts by the loss of 2 molecules of water, and are capable of reconversion into those salts. It will be remembered that many of these nitriles are identical with the cyanides of the alcohol-radicals.

Oxalonitrile,	NC	$=$	Cy, cyanogen.	
Formonitrile,	NCH	$=$	HCy, hydrocyanic acid.	
Acetonitrile,	NC_2H_3	$=$	$CH_3.CN$, cyanide of methyle.	
Propionitrile,	NC_3H_5	$=$	$C_2H_5.CN$,,	ethyle.
Benzonitrile,	NC_7H_5	$=$	$C_6H_5.CN$,,	phenyle.

A by no means numerous class of substances, frequently spoken of as

the *imides*,* are obtained by the action of heat upon the acid ammonia salts of certain bibasic acids, by the loss of two molecules of water, thus—



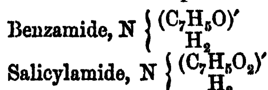
$$NH_4HC_{10}H_{14}O_4 - 2H_2O = NH.C_{10}H_{14}O_2.$$

Bicamphorate of ammonia. Camphorimide.

395. If the amides be regarded as immediately derived from ammonia by substitution, their want of alkaline properties must be ascribed to the introduction of an electro-negative radical in place of the hydrogen.

Thus, if oxalic acid be regarded as $H_2(C_2O_2)O_2$, then oxamide may be viewed as a double molecule of ammonia, in which two atoms of hydrogen have been displaced by (C_2O_2); $N_2 \left\{ \begin{matrix} (C_2O_2)'' \\ H_4 \end{matrix} \right.$

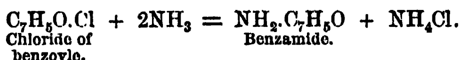
Again, if benzoic acid and salicylic acid, respectively, be regarded as $(C_7H_5O)HO$ and $(C_7H_5O_2)HO$, then their amides would be represented as—



Benzamide, $N \left\{ \begin{matrix} (C_7H_5O)' \\ H_2 \end{matrix} \right.$

Salicylamide, $N \left\{ \begin{matrix} (C_7H_5O_2)' \\ H_2 \end{matrix} \right.$

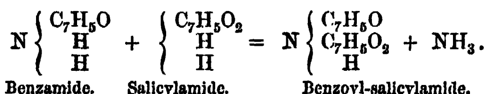
and it should be possible to procure them from ammonia by processes similar to that which furnishes ethylamine, &c. It is found that when chloride of benzoyle is heated with ammonia, benzamide is really produced—



$$C_7H_5O.Cl + 2NH_3 = NH_2.C_7H_5O + NH_4Cl.$$

Chloride of benzoyle. Benzamide.

But we ought also to be able to carry the substitution farther by displacing the remaining hydrogen; accordingly, when benzamide and salicylamide are heated together, ammonia is disengaged, and benzoyl-salicylamide obtained—

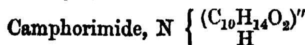


$$N \left\{ \begin{matrix} C_7H_5O \\ H \\ H \end{matrix} \right. + \left\{ \begin{matrix} C_7H_5O_2 \\ H \\ H \end{matrix} \right. = N \left\{ \begin{matrix} C_7H_5O \\ C_7H_5O_2 \\ H \end{matrix} \right. + NH_3.$$

Benzamide. Salicylamide. Benzoyl-salicylamide.

Amides have even been obtained in which the three atoms of hydrogen in ammonia are displaced by different radicals.

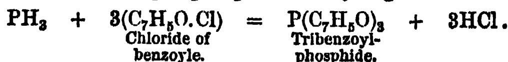
It is evident that the imides might be regarded as ammonias in which two atoms of hydrogen have been replaced by a diatomic radical, thus—



Camphorimide, $N \left\{ \begin{matrix} (C_{10}H_{14}O_2)'' \\ H \end{matrix} \right.$

and the nitriles, as ammonias in which all the hydrogen has been replaced by a triatomic radical, but experimental evidence is scarcely in favour of these views.

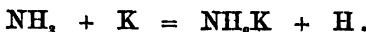
If the amides be really derivatives from ammonia, it would be expected that similar bodies should be derived from phosphuretted hydrogen (PH_3). An example of these is furnished by *tribenzoyl-phosphide*, $P(C_7H_5O)_3$, which is obtained by the action of chloride of benzoyle upon phosphuretted hydrogen.



$$PH_3 + 3(C_7H_5O.Cl) = P(C_7H_5O)_3 + 3HCl.$$

Chloride of benzoyle. Tribenzoyl-phosphide.

396. *Metal-amides.*—The possibility of substituting metals for the hydrogen in ammonia has only recently been fully established, though it had long been known that when potassium and sodium were heated in gaseous ammonia, hydrogen was evolved, and *potassamide* and *sodamide* were produced—



$$NH_3 + K = NH_2K + H.$$

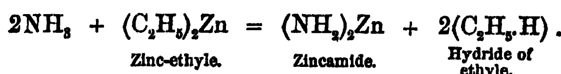
When potassamide is heated, ammonia is evolved, and *tripotassamide* (NK_3) produced—



$$3(NH_2K) = NK_3 + 2NH_3.$$

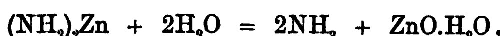
* This designation was originally employed upon the supposition that these bodies contain the imaginary radical imidogen, NH; and, in a similar manner, the amides were supposed to contain amidogen, NH_2.

If ammoniacal gas be passed into an ethereal solution of zinc-ethyle, hydride of ethyle is evolved, and a white amorphous precipitate of *zincamide* separates—



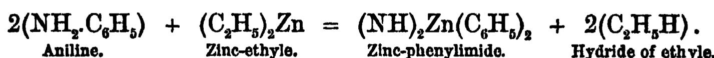
$$2NH_3 + (C_2H_5)_2Zn = (NH_2)_2Zn + 2(C_2H_5.H).$$

When zincamide is brought in contact with water, it is decomposed with evolution of heat, yielding hydrated oxide of zinc and ammonia—



$$(NH_2)_2Zn + 2H_2O = 2NH_3 + ZnO.H_2O.$$

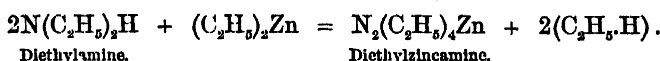
The decomposing action of zinc-ethyle upon the bases derived from ammonia is parallel with that upon ammonia itself. Thus, with aniline—



$$2(NH_2.C_6H_5) + (C_2H_5)_2Zn = (NH)_2Zn(C_6H_5)_2 + 2(C_2H_5H).$$

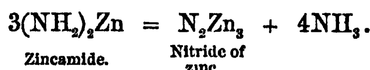
When the zinc-phenylimide is treated with water, of course aniline is reproduced.

When diethylamine is heated with zinc-ethyle—



$$2N(C_2H_5)_2H + (C_2H_5)_2Zn = N_2(C_2H_5)_4Zn + 2(C_2H_5.H).$$

When zincamide is heated above 400° F., it is decomposed into ammonia and *nitride of zinc* (N_2Zn_3), which represents ammonia, in which the three atoms of hydrogen are replaced by zinc—



$$3(NH_2)_2Zn = N_2Zn_3 + 4NH_3.$$

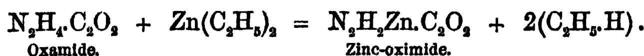
The nitride of zinc is a grey powder, which is unaffected by a red heat if air be excluded. If it be moistened with water, it becomes red hot, being decomposed with great violence, according to the equation—



$$N_2Zn_3 + 6H_2O = 2NH_3 + 3(ZnO.H_2O).$$

It might be anticipated that if the amides be truly formed after the ammonia-type, they should behave towards zinc-ethyle in the same manner as ammonia and aniline.

By heating oxamide with zinc-ethyle, two of its atoms of hydrogen may be replaced by zinc—



$$N_2H_4.C_2O_2 + Zn(C_2H_5)_2 = N_2H_2Zn.C_2O_2 + 2(C_2H_5.H).$$

In a similar manner, acetamide ($NH_2.C_2H_3O$) is converted into zinc-acetimide $N_2H_2Zn(C_2H_3O)_2$. These bodies are reconverted into their corresponding amides and oxide of zinc, when treated with water.

Derivatives of the Alcohols.

397. *Chloroform.*—Among the useful substances prepared from members of the alcohol series, *chloroform* ($CHCl_3$) occupies a prominent position.

It is prepared by distilling 1 part of alcohol with 6 parts of chloride of lime, and 24 parts of water, until about 1½ part has passed over; the distilled liquid, consisting chiefly of water and chloroform, separates

into two layers, the heavier being chloroform (sp. gr. 1·5). The upper aqueous layer having been drawn off by a siphon, the chloroform is shaken with oil of vitriol to remove certain volatile oils, which have distilled over with it, and as soon as it has risen to the surface of the oil of vitriol, it is drawn off and rectified by distillation, until it boils regularly at 142° F.

The chemical change involved in the preparation of chloroform appears to consist of two distinct stages, in the first of which the alcohol is converted into *chloral* by the action of the chlorine furnished by the chloride of lime, $\underset{\text{Alcohol.}}{C_2H_6O} + Cl_8 = \underset{\text{Chloral.}}{C_2HCl_3O} + 5HCl$; the hydrochloric acid is, of course, neutralised by the lime. In the second stage the chloral is acted upon by the hydrate of lime, which is always present in commercial chloride of lime, and is converted into chloroform and formiate of lime,

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + CaO.H_2O = \underset{\text{Formiate of lime.}}{Ca(CHO_2)_2} + \underset{\text{Chloroform.}}{2CHCl_3}.$$

Chloroform is remarkable for its very fragrant odour, and for the power of its vapour to produce insensibility to pain, for which purpose it is often used in surgical operations. This property is not peculiar to chloroform, but is possessed in different degrees by most other liquids of powerful ethereal odour, such as ordinary ether, bisulphide of carbon, bichloride (tetrachloride) of carbon, &c. Chloroform is also used for dissolving caoutchouc, which it takes up more readily and abundantly than any other liquid, and is employed for extracting the poisonous alkaloids (particularly strychnine), when mixed with organic matters. The name chloroform has been conferred upon this substance on the supposition that it contained the radical of formic acid (formyle CH), and it is sometimes styled the *terchloride of formyle.* This belief is encouraged by its behaviour with an alcoholic solution of potash, when it yields formiate of potash and chloride of potassium—



$$\underset{\text{Chloroform.}}{CHCl_3} + 4KHO = \underset{\text{Formiate of potash.}}{KCHO_2} + 3KCl + 2H_2O.$$

But the processes by which it may be formed would lead us to regard it as a substitution-product from marsh-gas (hydride of methyle, $CH_3.H$). If marsh-gas be diluted with an equal volume of carbonic acid, and to 1 volume of this mixture at least 1½ volume of chlorine be added, chloroform is slowly produced, $CH_4 + Cl_6 = 3HCl + CHCl_3$. Chloroform is also formed by the action of chlorine upon chloride of methyle—



$$CH_3Cl + Cl_4 = CHCl_3 + 2HCl.$$

Wood-spirit (hydrated oxide of methyle) may be employed instead of alcohol for the preparation of chloroform.

If chloroform be distilled in a current of chlorine, it is converted into tetrachloride of carbon, $CHCl_3 + Cl_2 = CCl_4 + HCl$. When chloroform is heated with amalgam of potassium, acetylene (C_2H_2) is disengaged, which is polymeric with the hypothetical radical formyle CH.

Bromoform ($CHBr_3$) and *Iodoform* (CHI_3) have no practical interest.

Chloral ($CHCl_3O$), which has been mentioned as resulting from the action of chlorine upon alcohol, may be regarded as aldehyde (C_2H_4O), in which 3 atoms of hydrogen are replaced by chlorine.

It is prepared by passing thoroughly dried chlorine into absolute

alcohol, which must be placed in a vessel surrounded by cold water at the commencement, because the absorption of chlorine is attended by great evolution of heat. The passage of chlorine is continued for many hours, and when the absorption takes place slowly, the alcohol is gradually heated to boiling, the chlorine being still passed in until the liquid refuses to absorb it. The principal reaction is C_2H_6O (*alcohol*) + Cl_8 = C_2HCl_3O (*chloral*) + 5HCl.* But a secondary reaction takes place between the hydrochloric acid and the alcohol; $(C_2H_5)HO$ (*alcohol*) + HCl = H_2O + $(C_2H_5)Cl$ (*hydrochloric ether*). The water thus formed combines with the chloral, forming a heavy oily liquid, which solidifies on standing to a white crystalline mass of *chloral hydrate*, $C_2HCl_3O.H_2O$. To obtain chloral itself, this must be distilled with twice its volume of oil of vitriol to remove the water, and with quick-lime to remove the hydrochloric acid.

Chloral is a colourless liquid, with a peculiar pungent odour, exciting to tears. Its sp. gr. is 1·5, and it boils at 201° F. It makes a greasy mark on paper, and mixes with water, alcohol, and ether.

When mixed with a small quantity of water, combination takes place, with evolution of heat, and the crystallised hydrate is produced. Exposed to moist air, it absorbs water and forms the hydrate. The chloral-hydrate itself readily absorbs water from the air; it may be sublimed without decomposition.

When kept, chloral suffers a change somewhat resembling that of aldehyde, becoming an opaque white mass, *insoluble chloral*, insoluble in water, alcohol, and ether, and reconvertible into liquid chloral by distillation. Left in contact with water, it becomes gradually converted into chloral hydrate. Chloral is decomposed by solution of potash; C_2HCl_3O (*chloral*) + KHO = $KCHO_2$ (formiate of potash) + $CHCl_3$ (chloroform).

Chloral hydrate has been lately much used medicinally for procuring sleep. The distillation of starch or sugar with hydrochloric acid and binoxide of manganese furnishes chloral, together with other products.

398. *Perfume-ethers.*—Certain of the compound ethers, formed by the combination of oxide of ethyle and its analogues with the acids of the acetic series, are employed in perfumery and confectionery.

Thus, the *butyrate of ethyle*, or *butyric ether* ($C_2H_5.C_4H_7O_2$), prepared by distilling butyrate of potash with alcohol and sulphuric acid, has a decided flavour of pine apples. *Acetate of amyle* ($C_5H_{11}.C_2H_3O_2$) has a very strong resemblance in taste and smell to the jargonelle pear; it is obtained by distilling fousel oil (hydrated oxide of amyle) with acetate of soda and sulphuric acid.

The *valerianate of amyle*, which has the flavour of apples, and is known as *apple-oil*, is obtained by distilling fousel oil with sulphuric acid and bichromate of potash, when the chromic acid of the latter oxidises one portion of the hydrate of amyle ($C_5H_{11}.HO$), converting it into valerianic acid ($C_5H_{10}O_2$), which then forms the valerianate of amyle ($C_5H_{11}.C_5H_9O_2$).

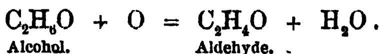
399. Aldehydes— *Vinic or acetic aldehyde.*—It has been already noticed (p. 487) that a considerable loss of alcohol has occasionally taken place in the manufacture of vinegar, in consequence of the formation of aldehyde

* An intermediate compound of chloral and alcohol, $C_2HCl_3O.C_2H_6O$, also appears to be formed. It is a solid crystalline body, fusing at 115° F., boiling at 234° F., and difficultly soluble in water, which distinguishes it from chloral hydrate. Heat decomposes it into chloral and alcohol.

(C_2H_4O) instead of acetic acid ($C_2H_4O_2$) by a partial oxidation of the alcohol. In order to prepare aldehyde in quantity, alcohol is distilled with sulphuric acid and binoxide of manganese, or with sulphuric acid and bichromate of potash, or it may be oxidised by chlorine in the presence of water.

Three parts of binoxide of manganese in fine powder are introduced into a retort, and a mixture of 3 parts of sulphuric acid and 2 of water, which has been allowed to cool, is poured upon it. 2 parts of alcohol (sp. gr. ·85) are then added, the mixture very gently heated, and the vapours condensed in a Liebig's condenser, or in a worm (fig. 214) supplied with iced water. If bichromate of potash be employed, 3 parts of the salt are introduced into the retort with 2 parts of alcohol. The retort is placed in cold water to moderate the action, and a mixture of 4 parts of sulphuric acid with three times its volume of water is allowed to flow slowly into the retort. A very gentle heat may be applied when the action has moderated.

In these processes the alcohol is oxidised according to the equation—

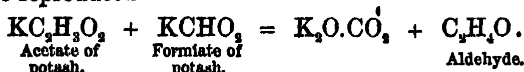


$$\underset{\text{Alcohol.}}{C_2H_6O} + O = \underset{\text{Aldehyde.}}{C_2H_4O} + H_2O.$$

In the first process the oxygen is derived from the binoxide of manganese, leaving sulphate of manganese ($MnO.SO_3$) in the retort; in the second process, the chromic acid of the bichromate furnishes the oxygen, sulphate of chromium ($Cr_2O_3.3SO_3$) being formed. As might be expected, a portion of the alcohol is oxidised to a higher degree, and converted into acetic acid ($C_2H_4O_2$), so that some acetic ether comes over together with the aldehyde. Another product, *acetal*, is also found in the distillate, which has the composition $C_6H_{14}O_2$, and may be regarded as resulting from the union of ether, formed by a secondary action of the sulphuric acid upon the alcohol, with aldehyde ($(C_2H_5)_2O.C_2H_4O$).

By redistilling the aldehyde with an equal weight of fused chloride of calcium in a gently heated water-bath, it may be freed from most of the water and alcohol, which are left behind in the retort, the boiling point of aldehyde being only 67°·8 F. After rectification, it may be separated from the acetic ether and acetal, by taking advantage of its property of combining with ammonia to form a compound which is insoluble in ether; the rectified aldehyde is mixed with twice its volume of ether, placed in a bottle surrounded by ice, and saturated with gaseous ammonia (p. 120), when white needle-like crystals of *aldehyde ammonia* ($NH_3.C_2H_4O$) are deposited. By distilling this compound with diluted sulphuric acid, and condensing the vapour in a thoroughly cooled receiver, pure aldehyde is obtained, from which the last portions of water may be removed by standing over fused chloride of calcium and a final distillation.

Aldehyde may be recognised by its peculiar acrid odour, which affects the eyes, as well as by its volatility and inflammability. It absorbs oxygen from air even at the ordinary temperature, and is gradually converted into acetic acid. Its attraction for oxygen enables it to reduce the salts of silver to the metallic state, and a characteristic test for aldehyde consists in adding a little nitrate of silver and a trace of ammonia; on heating, the silver is deposited as a mirror on the sides of the test-tube. In contact with hydrate of potash, aldehyde undergoes decomposition, yielding a brown substance (*resin of aldehyde*) and a solution of acetate and formiate of potash. By distilling a mixture of these two salts, aldehyde may be reproduced—



$$\underset{\text{Acetate of potash.}}{KC_2H_3O_2} + \underset{\text{Formiate of potash.}}{KCHO_2} = K_2O.CO_2 + \underset{\text{Aldehyde.}}{C_2H_4O}.$$

These reactions lend some support to the opinion, that aldehyde should be represented as being framed upon the model of a molecule of hydrogen (HH), in which the place of one atom of hydrogen is occupied by *acetyle*

(C_2H_3O), the hypothetical radical of acetic acid. For if formiate of potash be distilled with caustic potash, it yields carbonate of potash and two atoms of hydrogen, $KCHO_2 + KHO = K_2O.CO_2 + HH$; and if acetate of potash be employed instead of the hydrate, aldehyde is obtained instead of hydrogen—



$$KCHO_2 + K(C_2H_3O)O = K_2O.CO_2 + (C_2H_3O)H.$$

On this view it is easy to explain the tendency of aldehyde to undergo oxidation, forming acetic acid, just as hydrogen is converted into water by oxidation.

Type.—Molecule of hydrogen, H.H Aldehyde (hydride of acetyle), $C_2H_3O.H$	*Type.*—Molecule of water, H_2O Acetic acid, $(C_2H_3O)HO$.

As might be anticipated, it is found that when vapour of aldehyde is passed over heated caustic potash (mixed with lime) it yields acetate of potash and hydrogen, $C_2H_3O.H + KHO = H.H + K(C_2H_3O)O$.

By the action of potassium, the atom of hydrogen may be displaced from the aldehyde, and the compound $(C_2H_3O)K$ obtained.

In contact with water and sodium amalgam, aldehyde combines with the nascent hydrogen, and produces alcohol. Chlorine displaces three-fourths of the hydrogen from aldehyde, producing *chloral*, C_2Cl_3HO, which has been already noticed as yielding chloroform when acted on by alkalies.

Perfectly pure aldehyde cannot be kept for any length of time, even in sealed tubes, since it becomes converted into *metaldehyde* and *elaldehyde*, which have the same composition as aldehyde, but differ widely from it in properties, metaldehyde being a crystalline solid, and elaldehyde a liquid, boiling at 201° F. The true formula of elaldehyde would appear to be $C_6H_{12}O_3$ for the specific gravity of its vapour is 4·52, or three times that of aldehyde vapour (1·53). Metaldehyde is reconverted into aldehyde when heated to 400° F. in a sealed tube.

When aldehyde is treated with a saturated solution of bisulphite of soda ($Na_2O.H_2O.2SO_2$), it forms a crystalline compound, which is soluble in water, but insoluble in the saline solution, and contains the elements of 2 molecules of the aldehyde and 1 molecule of the bisulphite.

If the view above referred to be correct, which represents aldehyde as the hydride of acetyle (the radical of acetic acid), each of the acids belonging to the acetic series would be expected to have a corresponding aldehyde. Accordingly, just as acetate of lime, when distilled with formiate of lime, yields acetic aldehyde, so valerianic, œnanthic, and caprylic aldehydes may be obtained by distilling the corresponding lime-salts with formiate of lime.

The chief aldehydes of this series which have at present been examined are—

Acetic aldehyde, ...	C_2H_4O*
Propionic aldehyde, . .	C_3H_6O
Butyric aldehyde, ...	C_4H_8O
Valeric aldehyde, . . .	$C_5H_{10}O$

* It will be remarked that these aldehydes are polymeric with the compound ethers formed by their acids; thus, acetic aldehyde is polymeric with acetic ether, for—



$$2C_2H_4O = C_2H_5.C_2H_3O_2,$$

but the sp. gr. of aldehyde vapour (1·53) is only half that of acetic ether vapour (3·06).

Œnanthic aldehyde, . .	$C_7H_{14}O$
Caprylic aldehyde, . .	$C_8H_{16}O$
Rutic aldehyde, . . .	$C_{10}H_{20}O$
Euodic aldehyde, . . .	$C_{11}H_{22}O$
Lauric aldehyde, . . .	$C_{12}H_{24}O$

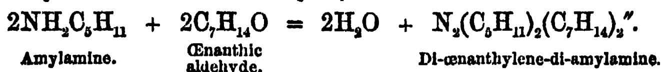
The radicals corresponding to acetyle, which may be regarded as associated with hydrogen in these aldehydes, have not, for the most part, been isolated; a substance having the same composition as butyryle (C_4H_7O), the supposed radical of butyric acid ($C_4H_8O_2$), has, however, been obtained from that acid by an indirect process.

Acetic, propionic, and butyric aldehydes have been found among the products of the oxidising action of a mixture of binoxide of manganese and sulphuric acid upon fibrine, albumen, and caseine.

Valeric aldehyde is obtained, like acetic aldehyde, by distilling the corresponding alcohol (amyle-alcohol, $C_5H_{12}O$) with sulphuric acid and bichromate of potash.

Capric (rutic), euodic, and lauric aldehydes are found in essential oil of rue. The higher aldehydes of the series are not so easily oxidised as those containing a lower number of carbon atoms.

When an aldehyde is heated with one of the bases derived from ammonia by the substitution of an alcohol-radical for one atom of hydrogen, the other two atoms of hydrogen of the ammonia are replaced by the diatomic hydrocarbon of the aldehyde; thus—



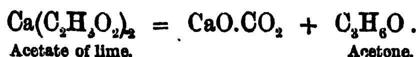
$$2NH_2C_5H_{11} + 2C_7H_{14}O = 2H_2O + N_2(C_5H_{11})_2(C_7H_{14})_2''.$$

Amylamine. Œnanthic aldehyde. Di-œnanthylene-di-amylamine.

This reaction has been recommended for the determination of the replaceable (or typical) hydrogen in organic bases.

400. Acetones.—If the lime salts of the acids of the acetic series, instead of being distilled with formiate of lime, as for the preparation of the aldehydes, be distilled alone, or with quick-lime, a series of homologous products is obtained, each of which is isomeric with the aldehyde of the series next below it in the table, though totally different from that aldehyde in properties.

Thus, by distilling acetate of lime with lime, the liquid *acetone* or *pyro-acetic spirit* (C_3H_6O) is obtained, which has been already noticed among the products of the distillation of wood—



$$Ca(C_2H_3O_2)_2 = CaO.CO_2 + C_3H_6O.$$

Acetate of lime. Acetone.

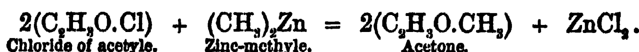
Acetone has the same composition as propionic aldehyde.* By similar processes the following acetones (or *ketones*, as they are frequently called) have been obtained:—

Acetone, . . .	C_3H_6O
Propione, . . .	$C_5H_{10}O$
Butyrone, . . .	$C_7H_{14}O$
Valerone, . . .	$C_9H_{18}O$.

These substances are allied, in some of their properties, to the aldehydes, especially in forming crystalline compounds with bisulphite of soda. Hence many chemists have been led to believe that they are composed,

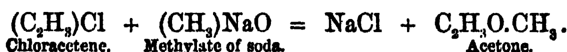
* Aldehyde is slowly formed by the action of chromic acid upon ethylene, and acetone may be obtained in a similar manner from propylene.

like the aldehydes, after the model of a molecule of hydrogen, but that in the acetones the radicals of the corresponding acids are associated, not with an atom of hydrogen, but with the hydrocarbon radical of the next lower alcohol. Thus, the acetone of the acetic series (C_3H_6O) would be composed of the radical acetyle (C_2H_3O) associated with methyle (CH_3), and this view of its constitution is supported by the formation of acetone, when chloride of acetyle is acted upon by zinc-methyle—



$$\underset{\text{Chloride of acetyle.}}{2(C_2H_3O.Cl)} + \underset{\text{Zinc-methyle.}}{(CH_3)_2Zn} = \underset{\text{Acetone.}}{2(C_2H_3O.CH_3)} + ZnCl_2.$$

In a similar manner, chloracetene (resulting from the action of chlorocarbonic acid on aldehyde) yields acetone when acted on by methylate of soda (sodium-methyle-alcohol)—



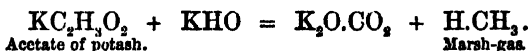
$$\underset{\text{Chloracetene.}}{(C_2H_3)Cl} + \underset{\text{Methylate of soda.}}{(CH_3)NaO} = NaCl + \underset{\text{Acetone.}}{C_2H_3O.CH_3}.$$

Further corroboration is obtained by distilling a mixture of equivalent quantities of acetate and valerianate of potash, when an acetone is obtained, which contains valeryle (C_5H_9O), associated with methyle (CH_3)—



$$\underset{\text{Acetate of potash.}}{KC_2H_3O_2} + \underset{\text{Valerianate of potash.}}{KC_5H_9O_2} = K_2O.CO_2 + C_5H_9O.CH_3.$$

It will be remembered that when acetate of potash is distilled with caustic potash, it yields marsh-gas by a precisely parallel reaction—

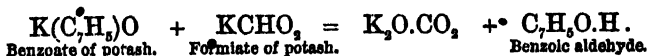


$$\underset{\text{Acetate of potash.}}{KC_2H_3O_2} + KHO = K_2O.CO_2 + \underset{\text{Marsh-gas.}}{H.CH_3}.$$

Acetone may also be prepared by distilling sugar with eight times its weight of quick-lime, when it is accompanied by another liquid, *metacetone*, $C_6H_{10}O$, which differs from acetone in being insoluble in water. When this liquid is heated with bichromate of potash and sulphuric acid, it is oxidised and converted into *metacetonic* or *propionic acid*, $HC_3H_5O_2$, which may also be produced by the oxidation of acetone.

401. The description above given of the properties of aldehyde will have recalled those of some of the essential oils containing oxygen. Thus, essential oil of bitter almonds (C_7H_6O), when exposed to air, absorbs oxygen, and is converted into benzoic acid ($C_7H_6O_2$), just as aldehyde (C_2H_4O) passes into acetic acid ($C_2H_4O_2$). Moreover, oil of bitter almonds forms a crystalline compound with bisulphite of soda, similar to that formed by aldehyde, and its conversion into this compound is sometimes resorted to in order to obtain the pure oil.

In constitution, also, oil of bitter almonds (hydride of benzoyle, $C_7H_5O.H$) closely resembles aldehyde (hydride of acetyle, $C_2H_3O.H$), and just as the latter may be obtained by distilling acetate of potash with formiate of potash, so benzoic aldehyde (oil of bitter almonds) may be obtained from benzoate of potash.

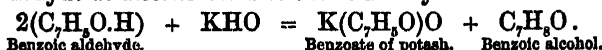


$$\underset{\text{Benzoate of potash.}}{K(C_7H_5)O} + \underset{\text{Formiate of potash.}}{KCHO_2} = K_2O.CO_2 + \underset{\text{Benzoic aldehyde.}}{C_7H_5O.H}.$$

Oil of bitter almonds is produced, together with some aldehydes of the acetic series of acids (p. 547), when certain albuminous bodies are oxidised by sulphuric acid and binoxide of manganese.

When benzoic aldehyde is acted on by an alcoholic solution of caustic

potash, an oily liquid is obtained, which stands in the same relation to benzoic aldehyde as alcohol bears to acetic aldehyde.



$$2(C_7H_5O.H) + KHO = K(C_7H_5O)O + C_7H_8O.$$

Benzoic aldehyde. Benzoate of potash. Benzoic alcohol.

The conversion of bitter almond oil into benzoic alcohol may also be effected by the action of water and amalgam of sodium (to furnish nascent hydrogen); whereas, by treatment with zinc and hydrochloric acid, it is converted into *hydrobenzoine* (C_7H_7O).

The hydrochloric ether of benzoic alcohol, C_7H_7Cl, is sometimes called *chloride of benzyle*, the radical *benzyle*, C_7H_7, being supposed to have the same relation to the benzoic series as ethyle has to the acetic series. By the action of ammonia upon chloride of benzyle, *benzylamine*, $NH_2(C_7H_7)$, and *tri-benzylamine*, $N(C_7H_7)_3$, have been obtained; the former is isomeric with toluidine, but is by no means identical with it; for benzylamine is a liquid having basic properties far more powerful than those of toluidine, and it is very readily soluble in water, which dissolves but little of the latter base.

The benzoic acetone or *benzone* ($C_{13}H_{10}O$) has been obtained by the distillation of benzoate of lime. It is often called *benzophenone*, being regarded as an association of benzoyle with phenyle, $C_7H_5O.C_6H_5$; for when distilled with potash, it yields benzoate of potash and benzole (hydride of phenyle)—



$$C_7H_5O.C_6H_5 + KHO = K(C_7H_5O)O + C_6H_5.H.$$

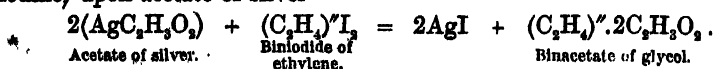
Benzophenone. Benzoate of potash. Benzole.

Oil of cinnamon (p. 471) or hydride of cinnamyle ($C_9H_7O.H$) is the aldehyde of cinnamic acid ($C_9H_8O_2$); and essential oil of cummin contains the aldehyde ($C_{10}H_{11}O.H$) of cuminic acid ($C_{10}H_{12}O_2$), and yields cuminic alcohol ($C_{10}H_{14}O$) when treated with alcoholic solution of potash. Oil of spiræa or hydride of salicyle ($C_7H_5O_2.H$) is the aldehyde of salicylic acid ($C_7H_6O_3$). Hydride of anisyle ($C_8H_7O_2.H$), obtained by the oxidation of oil of aniseed, is the aldehyde of anisic acid ($C_8H_8O_3$), and of anisic alcohol ($C_8H_{10}O$). These aldehydes allow their associated atom of hydrogen to be displaced by chlorine more readily than the aldehydes of the acetic series, to form chlorides of their respective radicals (p. 470).

Glycol—Polyatomic Alcohols.

402. It has been already shown (p. 518) that alcohol may be conveniently regarded as composed after the fashion of a molecule of water (H_2O) in which half the hydrogen has been displaced by ethyle (C_2H_5); according to this view alcohol is represented by the formula $H(C_2H_5)O$; and it is a *monatomic* alcohol, for it contains the monatomic radical $(C_2H_5)'$. But if, following the same plan, a diatomic radical, such as ethylene $(C_2H_4)''$, were to displace half the hydrogen in water, the displacement could not be effected in less than two molecules of water (H_4O_2), and a *diatomic alcohol* would result.

Glycol ($C_2H_6O_2$) is the representative of the diatomic alcohols, and may be regarded as two molecules of water, in which half the hydrogen is replaced by ethylene ($H_2(C_2H_4)''O_2$). It is obtained by the action of biniodide of ethylene (formed by the direct union of olefiant gas with iodine) upon acetate of silver—



$$2(AgC_2H_3O_2) + (C_2H_4)''I_2 = 2AgI + (C_2H_4)''.2C_2H_3O_2.$$

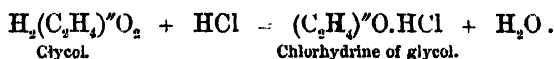
Acetate of silver. Biniodide of ethylene. Binacetate of glycol.

The binacetate of glycol thus formed corresponds to the acetic ether $((C_2H_5)C_2H_3O_2)$ derived from common alcohol; but since ethylene is diatomic, it displaces the hydrogen in two molecules of acetic acid. When the result of this action is distilled, the binacetate of glycol passes over as a colourless liquid, which sinks in water, and boils at 365° F.*

Glycol can be obtained from the binacetate by digesting it with hydrate of potash for some time at 360° F., and distilling, when the glycol passes over, its boiling point being 387° F. It is a colourless liquid, having a sweet taste, whence it derives its name (γλυκὺς, *sweet*). Like common alcohol, it mixes with water in all proportions, and may be distilled without decomposition. It also gives an inflammable vapour, and has never been frozen; but, unlike alcohol, it is heavier than water (sp. gr. 1·125), and does not mix with ether, though alcohol dissolves it readily.

Glycol is also capable of forming the *monacetate of glycol*, $C_2H_4HC_2H_3O_2$, and a remarkable compound has been obtained known as *acetobutyrate of glycol* $C_2H_4.C_2H_3O_2.C_4H_7O_2$.

The action of hydrochloric acid upon glycol does not perfectly correspond with its action upon common alcohol, for instead of yielding a chloride of ethylene, it gives a compound of hydrochloric acid with oxide of ethylene.

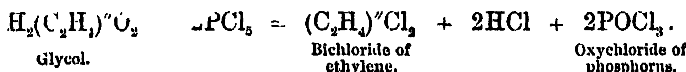


$$H_2(C_2H_4)''O_2 + HCl = (C_2H_4)''O.HCl + H_2O.$$

Glycol. Chlorhydrine of glycol.

By decomposing this compound with potash, the oxide of ethylene $(C_2H_4)''O$ is obtained, as a colourless liquid, which boils at 56° F., and is, therefore, not identical with aldehyde (which boils at 68° F.), though it has the same composition. It is obvious that glycol might be represented as $(C_2H_4)''O.H_2O$, the hydrated oxide of ethylene, and this view is favoured by the circumstance that glycol may be formed by heating the oxide of ethylene with water in a sealed tube; but, on the other hand, when glycol is treated with chloride of zinc, to dehydrate it, ordinary aldehyde (C_2H_4O), and not the ethylenic oxide, is produced.

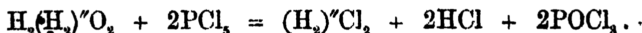
By the action of pentachloride of phosphorus upon glycol, the bichloride of ethylene, or Dutch liquid, is obtained—



$$H_2(C_2H_4)''O_2 \quad 2PCl_5 = (C_2H_4)''Cl_2 + 2HCl + 2POCl_3.$$

Glycol. Bichloride of ethylene. Oxychloride of phosphorus.

It will be observed that this equation is the exact counterpart of that which represents the action of pentachloride of phosphorus upon water, substituting diatomic ethylene for monatomic hydrogen—



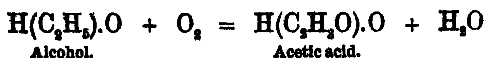
$$H_2(H_2)''O_2 + 2PCl_5 = (H_2)''Cl_2 + 2HCl + 2POCl_3.$$

Sodium acts upon glycol in the same manner as upon ordinary alcohol, but in consequence of the di-atomic character of glycol, the reaction takes place in two stages, producing, successively, *mono-sodium glycol*, $HNa(C_2H_4)''O_2$ and *di-sodium glycol*, $Na_2(C_2H_4)''O_2$, both which are solid.

When glycol is exposed to the action of oxygen in the presence of platinum-black, or when it is cautiously oxidised with nitric acid, it becomes converted into *glycolic acid*, $C_2H_4O_3$, which bears the same rela-

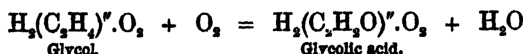
* A liquid isomeric with binacetate of glycol, but boiling at 336° F., is obtained by heating aldehyde in a sealed tube with acetic anhydride.

tion to it as acetic acid bears to common alcohol, as will be evident from the following equations :*—



$$H(C_2H_5).O + O_2 = H(C_2H_3O).O + H_2O$$

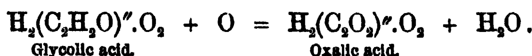
Alcohol. Acetic acid.



$$H_2(C_2H_4)''.O_2 + O_2 = H_2(C_2H_2O)''.O_2 + H_2O$$

Glycol. Glycolic acid.

in which the change consists, in both cases, in the substitution of O for H_2 in the radical of the alcohol, acetic acid being formed upon the type of a molecule of water (H_2O) in which H is replaced by C_2H_3O, and glycolic acid upon the type of two molecules (H_4O_2), in which H_2 are replaced by C_2H_2O. If the oxidation with nitric acid be carried farther, the remainder of the hydrogen in this last radical is replaced by oxygen, and oxalic acid is produced—



$$H_2(C_2H_2O)''.O_2 + O = H_2(C_2O_2)''.O_2 + H_2O.$$

Glycolic acid. Oxalic acid.

By the action of nascent hydrogen upon oxalic acid, the O in the radical may be again displaced by H_2, so that glycolic acid is reproduced.

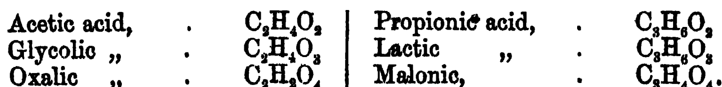
Glycolic acid forms a syrupy liquid which resembles lactic acid, but is distinguished from it by being precipitated with acetate of lead. Unlike oxalic acid, glycolic is a monobasic acid, only one atom of its hydrogen being replaceable by a metal. Glycolic acid is found together with oxalic acid among the products of the action of nitric acid upon alcohol in the preparation of fulminate of mercury, which is easily accounted for by the connection between alcohol and ethylene, which is best exhibited by writing the formula of alcohol $(C_2H_4).H_2O$.

Glycolic acid is the first member of a series of homologous acids, of which the most important is lactic acid, these acids standing in the same relation to the glycols in which the members of the acetic series stand to the alcohols.

Lactic Series of Acids.

Name.	Formula	Source.
Glycolic acid, .	$C_2H_4O_3$	Oxidation of glycol and of alcohol.
Lactic acid, . .	$C_3H_6O_3$	Fermentation of cane and milk sugars.
Butylactic acid,	$C_4H_8O_3$	Oxidation of butyl-glycol.
Valerolactic acid,	$C_5H_{10}O_3$	Decomposition of bromo-valerianic acid with oxide of silver.
Leucic acid, . .	$C_6H_{12}O_3$	Action of nitric acid on leucine.

It will be observed that these acids are intermediate, with respect to the number of atoms of oxygen which they contain, between the acetic and the oxalic series of acids; thus—



Acetic acid, .	$C_2H_4O_2$	Propionic acid, .	$C_3H_6O_2$
Glycolic „ .	$C_2H_4O_3$	Lactic „ .	$C_3H_6O_3$
Oxalic „ .	$C_2H_2O_4$	Malonic, .	$C_3H_4O_4$.

* The aldehyde of glycol, *glyoxal*, $C_2H_2O_2$, is found among the products of the decomposition of nitrous ether in contact with water.

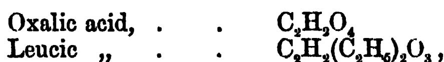
These three series of acids, therefore, present a relation to each other similar to that between the three series of alcohols, represented by—



Vinic alcohol, . .	C_2H_6O
Glycol, . . .	$C_2H_6O_2$
Glycerine, . .	$C_3H_8O_3$.

Just as acetic and glycolic acids are formed by the oxidation of alcohol and glycol, so the oxidation of glycerine by nitric acid furnishes *glyceric acid*, $C_3H_6O_4$.

The transition from the oxalic series to the lactic series of acids has been effected in the case of leucic acid, which has been artificially formed from oxalic acid, by converting it into oxalic ether, and acting upon this with zinc-ethyle, when leucic ether is obtained, from which leucic acid is easily prepared. The reaction is rendered intelligible if the two acids be thus formulated—

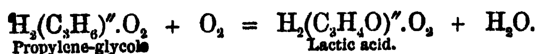


Oxalic acid, . .	$C_2H_2O_4$
Leucic „ . .	$C_2H_2(C_2H_5)_2O_3$,

from which it appears that, neglecting intermediate stages, the zinc of the zinc-ethyle removes an atom of oxygen from the oxalic acid, leaving ethyle in its stead, so that leucic acid may be regarded as *diethoxalic acid*, or oxalic acid containing two of ethyle instead of one of oxygen. If oxalate of methyle be substituted for oxalate of ethyle in this experiment, leucate of methyle, $CH_3.C_6H_{11}O_3$ is obtained, and when this is decomposed by baryta, and the leucate of baryta treated with sulphuric acid, fine crystals of leucic acid are obtained, which are readily soluble in water, alcohol, and ether, and sublime slowly at the ordinary temperature.* By the reaction between iodide of methyle, oxalate of methyle, and amalgamated zinc, *dimethoxalic acid*, $C_2H_2(CH_3)_2O_3$, has been obtained, which may be regarded as oxalic acid containing two of methyle in the place of an atom of oxygen. Dimethoxalic acid is isomeric with butylactic or acetonic acid ($C_4H_8O_3$); it crystallises in prisms resembling those of oxalic acid, which may be sublimed at 122° F., and volatilise slowly even at the ordinary temperature.

From the other hydrocarbons of the olefiant gas series (p. 508), glycols may be prepared by processes similar to that which furnishes ethylene-glycol. Thus propylene (C_3H_6) yields *propylene-glycol*, $H_2(C_3H_6)''.O_2$; butylene (C_4H_8), *butylene-glycol*, $H_2(C_4H_8)''.O_2$; amylene (C_5H_{10}), *amylene-glycol*, $H_2(C_5H_{10})''.O_2$; it is a very remarkable circumstance that the boiling points and specific gravities of these liquids *decrease* as the complexity of the formula *increases*, which is quite contrary to ordinary experience; thus amylene-glycol ($C_5H_{12}O_2$) has the sp. gr. 0·987, and boils at 351° F., whilst propylene-glycol ($C_3H_8O_2$) has the sp. gr. 1·051, and boils at 371° F.

When propylene-glycol is slowly oxidised, it is converted into *lactic acid*, exactly as glycol is converted into glycolic acid—



$$\underset{\text{Propylene-glycol}}{H_2(C_3H_6)''.O_2} + O_2 = \underset{\text{Lactic acid.}}{H_2(C_3H_4O)''.O_2} + H_2O.$$

The difference between the diatomic character of glycol and the monatomic character of ordinary alcohol, is strongly marked in their behaviour

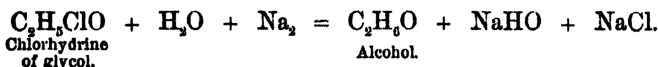
* It is said that this leucic acid, though closely resembling that obtained from oxalic ether, is not identical with it.

with the organic acids, for whilst the monatomic alcohol yields (with monobasic acids) only one series of compound ethers derived from one molecule of acid, the diatomic glycol yields two series derived respectively from one and two molecules of acid; thus we have monacetate of glycol $(C_2H_4)''.H(C_2H_3O)O_2$ and diacetate of glycol, $(C_2H_4)''.(C_2H_3O)_2.O_2$. In the last series, it is not necessary that the two molecules should consist of the same acid, as may be seen in the acetobutyrate of glycol, $(C_2H_4)''.C_2H_3O.C_4H_7O.O_2$.

Just as polyatomic ammonias are formed upon the type of several molecules of ammonia, so polyatomic alcohols may be produced by the substitution of compound radicals for hydrogen in a multiple alcohol type. Thus, by heating glycol in a sealed tube with oxide of ethylene, *di-ethylene-trialcohol*, $H_2(C_2H_4)''_2O_3$, is produced, which is formed upon the type of three molecules of alcohol, $H_3(C_2H_5)_3O_3$. In a similar manner, tri-ethylene-tetralcohol, $H_2(C_2H_4)_3''O_4$, is formed upon the quadruple alcohol type, $H_4(C_2H_5)_4O_4$.

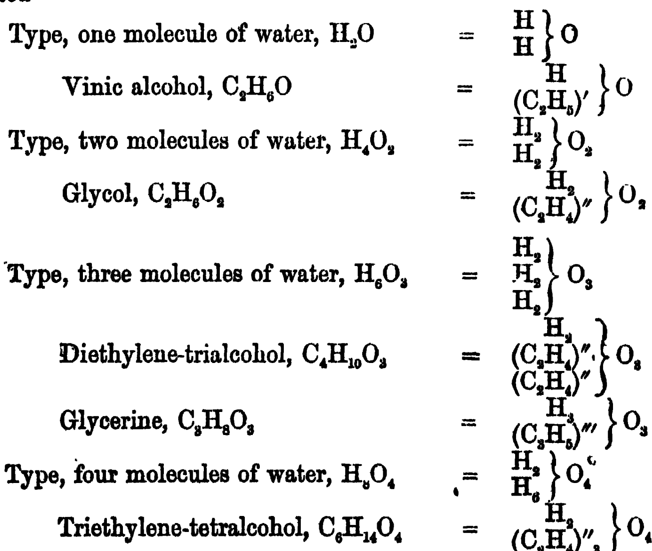
It will be seen hereafter that glycerine $(C_3H_8O_3)$, the sweet principle of oils and fats, is a triatomic alcohol, formed upon the type of three molecules of water (H_6O_3), in which half the hydrogen is replaced by the triatomic radical, $(C_3H_5)'''$, *glyceryle*, the formula of glycerine being $H_3(C_3H_5)'''O_3$.

It is easy to convert a diatomic into a monatomic alcohol; for example, if the chlorhydrine of glycol be treated with amalgam of sodium in the presence of water, it becomes converted into ordinary (monatomic) alcohol—



$$\underset{\text{Chlorhydrine of glycol.}}{C_2H_5ClO} + H_2O + Na_2 = \underset{\text{Alcohol.}}{C_2H_6O} + NaHO + NaCl.$$

The relation of the alcohols to water as their primary type is here exhibited—



Type, one molecule of water, H_2O	=	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$
Vinic alcohol, C_2H_6O	=	$\left.\begin{matrix}H\\(C_2H_5)'\end{matrix}\right\}O$
Type, two molecules of water, H_4O_2	=	$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$
Glycol, $C_2H_6O_2$	=	$\left.\begin{matrix}H_2\\(C_2H_4)''\end{matrix}\right\}O_2$
Type, three molecules of water, H_6O_3	=	$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}O_3$
Diethylene-trialcohol, $C_4H_{10}O_3$	=	$\left.\begin{matrix}H_2\\(C_2H_4)''\\(C_2H_4)''\end{matrix}\right\}O_3$
Glycerine, $C_3H_8O_3$	=	$\left.\begin{matrix}H_3\\(C_3H_5)'''\end{matrix}\right\}O_3$
Type, four molecules of water, H_8O_4	=	$\left.\begin{matrix}H_2\\H_6\end{matrix}\right\}O_4$
Triethylene-tetralcohol, $C_6H_{14}O_4$	=	$\left.\begin{matrix}H_2\\(C_2H_4)''_3\end{matrix}\right\}O_4$

The compounds formed by the action of acids upon these alcohols would then be represented by such formulæ as the following:—

Acetic ether, ...	$\left.\begin{matrix}(C_2H_3O)' \\ (C_2H_5)'\end{matrix}\right\} O$
Monacetate of glycol, . .	$\left.\begin{matrix}(C_2H_3O)'H \\ (C_2H_4)''\end{matrix}\right\} O_2$
Diacetate of glycol, ...	$\left.\begin{matrix}(C_2H_3O)_2' \\ (C_2H_4)''\end{matrix}\right\} O_2$
Acetobutyrate of glycol,	$\left.\begin{matrix}(C_2H_3O)' \\ (C_4H_7O)' \\ (C_2H_4)''\end{matrix}\right\} O_2$
Monacetine, ...	$\left.\begin{matrix}(C_2H_3O)'H_2 \\ (C_3H_5)'''\end{matrix}\right\} O_3$
Diacetine, ...	$\left.\begin{matrix}(C_2H_3O)_2'H \\ (C_3H_5)'''\end{matrix}\right\} O_3$
Triacetine, ...	$\left.\begin{matrix}(C_2H_3O)_3' \\ (C_3H_5)'''\end{matrix}\right\} O_3$

ACETIC ACID—THE FATTY ACID SERIES.

403. The most useful of the acids belonging to the acetic series (see p. 507) is acetic acid itself, the preparation of which has been already described.

Many of its salts are extensively employed in the arts. *Acetate of alumina* is used as a mordant by the dyer and calico-printer. *Acetate of lead* or *sugar of lead*, $Pb(C_2H_3O_2)_2$ 3Aq., is prepared by dissolving litharge (PbO) in an excess of acetic acid, when the solution deposits prismatic crystals of the acetate which are easily dissolved by water and alcohol.

Goulard's extract, or *tribasic acetate of lead*, is prepared by dissolving litharge in solution of acetate of lead; it may be obtained in needle-like crystals, which have the composition $Pb(C_2H_3O_2)_2 2PbO.H_2O$.

Verdigris, or *basic acetate of copper*, $Cu(C_2H_3O_2)_2.CuO.6H_2O$, is prepared by piling up sheets of copper with layers of fermenting husks of grapes (the marc of the wine-press), when the oxide of copper, formed at the expense of the oxygen of the air, combines with the acetic acid furnished by the oxidation of the alcohol.

Acetone (C_3H_6O) is obtained by the destructive distillation of acetate of lime—



$$\underset{\text{Acetate of lime.}}{Ca(C_2H_3O_2)_2} = CaO.CO_2 + \underset{\text{Acetone.}}{C_3H_6O}$$

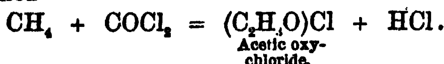
a decomposition which possesses some general interest since the lime-salts of the other acids of the acetic series yield *ketones* in a similar manner (see p. 548).

The acetone thus obtained is an ethereal liquid lighter than water, boiling at 133° F., and burning with a luminous flame. It is easily miscible with water, but separates when hydrate of potash is added, rising to the surface.

Under the action of chlorine, acetic acid loses an atom of hydrogen, taking chlorine in its place, and forming *chloracetic acid*, $H.C_2H_2ClO_2$;* and if the action be promoted by sun-light, *trichloracetic acid* may be formed, $H.C_2Cl_3O_2$, which may be crystallised. This latter acid has a peculiar interest on account of its being concerned in the production of acetic acid from inorganic materials, which was one of the first examples of the actual synthesis of organic compounds.

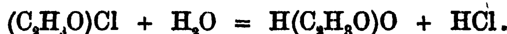
* *Dichloracetic acid*, $H.C_2HCl_2O_2$, has also been obtained.

The synthesis of acetic acid has been effected by the action of chloro-carbonic acid upon marsh-gas, when hydrochloric acid and acetic oxy-chloride are formed—



$$CH_4 + COCl_2 = \underset{\text{Acetic oxychloride.}}{(C_2H_3O)Cl} + HCl.$$

When the acetic oxychloride is decomposed by water, acetic acid is produced—

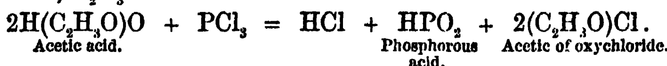


$$(C_2H_3O)Cl + H_2O = H(C_2H_3O)O + HCl.$$

This appears to be an example of a general method of synthesis of the volatile fatty acids, starting from the marsh-gas hydrocarbons derived from them; thus, hydride of amyle, C_5H_{12}, treated in a similar manner, yields caproic acid, $HC_6H_{11}O_2$.

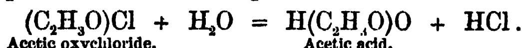
404. *Anhydrides of organic acids.—Acetic anhydride.*—The course of investigation by which, of late years, much light has been thrown upon the true constitution of acetic acid, and therefore of many other organic acids, is of a very instructive character. The strongest acetic acid which can be prepared (see p. 461) is known as *glacial acetic acid*, from its crystallising in icy leaflets at about 55° F. This acid has the composition $C_2H_4O_2$, and may be regarded as a molecule of water in which half the hydrogen is replaced by the hypothetical radical *acetyle*, C_2H_3O.

When this acid is distilled with terchloride of phosphorus, a colourless, very pungent liquid is obtained, which is commonly spoken of as *acetic oxychloride*, C_2H_3OCl—



$$\underset{\text{Acetic acid.}}{2H(C_2H_3O)O} + PCl_3 = HCl + \underset{\text{Phosphorous acid.}}{HPO_2} + \underset{\text{Acetic oxychloride.}}{2(C_2H_3O)Cl}.$$

That this acetic oxychloride (or *chloride of acetyle*) really bears a very close relationship to acetic acid, is shown by the action of water, which acts with explosive violence and reproduces the acetic acid—



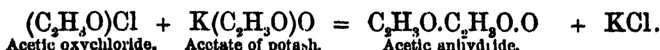
$$\underset{\text{Acetic oxychloride.}}{(C_2H_3O)Cl} + H_2O = \underset{\text{Acetic acid.}}{H(C_2H_3O)O} + HCl.$$

If caustic potash be allowed to act upon the chloride of acetyle—



$$(C_2H_3O)Cl + KHO = H(C_2H_3O)O + KCl.$$

But if acetate of potash ($KC_2H_3O_2$) be employed instead of caustic potash—



$$\underset{\text{Acetic oxychloride.}}{(C_2H_3O)Cl} + \underset{\text{Acetate of potash.}}{K(C_2H_3O)O} = \underset{\text{Acetic anhydride.}}{C_2H_3O.C_2H_3O.O} + KCl.$$

Acetic anhydride has also been obtained by heating dry acetate of lead or of silver with bisulphide of carbon in a sealed tube to about 320° F. for several hours, the tube being occasionally opened to relieve the pressure of the carbonic acid evolved—



$$2Pb(C_2H_3O)_2O_2 + CS_2 = 2PbS + CO_2 + 2(C_2H_3O)_2O.$$

The acetic anhydride is a neutral oily liquid which may be distilled off in the above experiment. Its smell recalls that of acetic acid, but affects the eyes strongly. It sinks in water, but dissolves slowly, with evolution of heat and formation of hydrated acetic acid.*

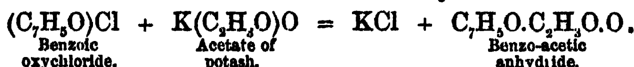
* If acetic anhydride be heated with an excess of binoxide of barium, it yields acetate of baryta, carbonic acid, and methyle gas (p. 513).



$$2(C_2H_3O)_2O + BaO_2 = Ba(C_2H_3O_2)_2 + 2CH_3 + 2CO_2.$$

By absorbing the carbonic acid with potash, the pure methyle gas is easily obtained.

The most convincing proof that this anhydride is really formed after the type of a molecule of water, is obtained by acting upon the acetate of potash with the benzoic instead of the acetic oxychloride—



$$\underset{\text{Benzoic oxychloride.}}{(C_7H_5O)Cl} + \underset{\text{Acetate of potash.}}{K(C_2H_3O)O} = KCl + \underset{\text{Benzo-acetic anhydride.}}{C_7H_5O.C_2H_3O.O}.$$

and the true nature of this double anhydride is seen by its conversion into a mixture of hydrated benzoic and acetic acids when left in contact with water.

By methods similar to that employed for acetic acid, the anhydrides of many other organic acids may be obtained—

Peroxides of organic radicals.—Considerable support has been offered to that view of the constitution of the organic acids, which represents them as composed after the type of water, by the discovery of certain compounds which bear the same relation to the anhydrides as peroxide of hydrogen bears to water.

When binoxide of barium is acted on by hydrochloric acid, chloride of barium and peroxide of hydrogen are formed—



$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

If binoxide of barium be acted on by benzoic oxychloride (chloride of benzoyle), the products are chloride of barium and *benzoic peroxide* (peroxide of benzoyle)—



$$BaO_2 + 2(C_7H_5O)Cl = BaCl_2 + (C_7H_5O)_2O_2.$$

The benzoic peroxide may be obtained in fine crystals from its ethereal solution, but like the peroxide of hydrogen, it is easily decomposed at about 212° F. with explosive violence. By the action of alkalies, it is resolved into benzoic acid and oxygen, just as peroxide of hydrogen yields water and oxygen—



$$(C_7H_5O)_2O_2 + 2KHO = 2K(C_7H_5O)O + O_2 + H_2O.$$

By acting upon acetic anhydride with binoxide of barium, the *acetic peroxide* (or peroxide of acetyle) is obtained—



$$BaO_2 + 2(C_2H_3O)_2O = \underset{\text{Acetate of baryta.}}{Ba(C_2H_3O_2)_2} + \underset{\text{Acetic peroxide.}}{(C_2H_3O)_2O_2}.$$

The acetic peroxide is an oily liquid, insoluble in water, and exploding with great violence when heated. It has the powerful oxidising properties which would be expected from its chemical resemblance to peroxide of hydrogen.

405. *Formic acid* ($H.CHO_2$) is regarded with great interest by the chemist, from its occurring both in the animal and vegetable kingdoms, and from the ease with which it may be artificially obtained. This acid is found in the leaves of stinging-nettles, and was originally obtained by distilling the red ants (*formica rufa*), whence it derives its name.

It has long been prepared in laboratories by the oxidation of various organic substances, particularly by distilling starch with binoxide of manganese and sulphuric acid. Another more modern process, which yields it more abundantly, consists in distilling dried oxalic acid with enough glycerine to cover it, when it is resolved into carbonic acid and formic acid—



$$H_2C_2O_4 \textit{ (Oxalic acid)} = HCHO_2 \textit{ (Formic acid)} + CO_2.$$

The glycerine appears to act by producing an unstable compound with the formic acid (analogous to the stearines and acetines, see p. 565), which is afterwards decomposed. The solution of formic acid thus obtained contains 75 per cent. of true hydrated formic acid. If dried oxalic acid be heated in the aqueous formic acid, and the solution allowed to crystallise, the oxalic acid retains the water, and when the liquid is decanted from the crystals and distilled, pure formic acid is obtained, and may be crystallised at a low temperature.

But the most remarkable method of obtaining formic acid is that in which it is formed from inorganic materials. When formic acid is heated with strong sulphuric acid, it is resolved into water and carbonic oxide, $HCHO_2 = H_2O + CO$.

It might, therefore, be expected to be reproducible by the combination of those two substances, and accordingly, if moistened caustic potash be heated for some hours to 212° F. in a flask filled with carbonic oxide, the gas is absorbed, and formiate of potash produced, from which the formic acid may be obtained by distillation with diluted sulphuric acid—



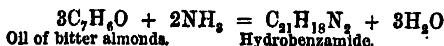
$$KHO + CO = KCHO_2 \text{ (Formiate of potash).}$$

This is a far simpler example of the synthesis of an organic compound from inorganic materials than that of acetic acid above referred to, and since the carbonic oxide may be prepared by heating carbonate of baryta with metallic iron, this method of synthesis is quite independent of any organic source of carbon. Ethylate of sodium, NaC_2H_5O, also absorbs carbonic oxide, forming *ethyl-formiate of sodium* $NaC(C_2H_5)O_2$ isomeric with propionate of soda, a little of this salt being also formed.

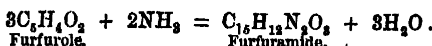
In properties, formic acid bears a great general resemblance to acetic acid, but has a more powerful action upon the skin when in the concentrated form. It is employed in the manufacture of one of the blue colours derived from coal-tar.

Furfurole ($C_5H_4O_2$), or oil of ants, accompanies the formic acid obtained by distilling amylaceous matters with binoxide of manganese and sulphuric acid. It is prepared in quantity by distilling bran (freed from starch and gluten by steeping in a cold weak solution of potash) with half its weight of sulphuric acid (previously diluted with an equal bulk of water), a current of steam being forced through the mixture; the furfurole distils over with the water, from which it may be separated by fractional distillation. It is a colourless oily substance, smelling of bitter almonds, becoming brown when exposed to the air, and but slightly soluble in water. Strong sulphuric acid dissolves it to a purple liquid, from which water precipitates it unchanged. Furfurole resembles the aldehydes in its property of reducing oxide of silver, and in forming a crystalline compound with bisulphite of soda. It is convertible by oxidation into pyromucic acid ($C_5H_4O_3$), the acid obtained by distilling the mucic acid derived from the oxidation of gum or milk-sugar. The systematic name for furfurole, therefore, would be *pyromucic aldehyde*.

Just as oil of bitter almonds (benzoic aldehyde), when acted on by ammonia, is converted into hydrobenzamide, so furfurole yields *furfuramide*—



$$\underset{\text{Oil of bitter almonds.}}{3C_7H_6O} + 2NH_3 = \underset{\text{Hydrobenzamide.}}{C_{21}H_{18}N_2} + 3H_2O$$

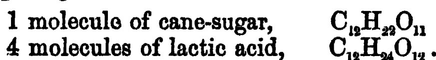


$$\underset{\text{Furfurole.}}{3C_5H_4O_2} + 2NH_3 = \underset{\text{Furfuramide.}}{C_{15}H_{12}N_2O_3} + 3H_2O.$$

And, just as hydrobenzamide, when boiled with solution of potash, yields the isomeric base *amarine* or *benzoline* ($C_{21}H_{18}N_2$), so furfuramide, when boiled with potash, gives *furfurine* ($C_{15}H_{12}N_2O_3$), which is isomeric with it.

Butyric acid ($HC_4H_7O_2$) is found not only in rancid butter, but in the juice of muscular flesh, and is a frequent product of fermentation.

Indeed, the best mode of obtaining this acid consists in exciting fermentation in sugar by contact with cheese; the liquid soon becomes acid, in consequence of the formation of *lactic acid* (the acid of sour milk), and if it be neutralised from time to time with chalk, this fermentation continues until the whole is converted into a pasty crystalline mass of lactate of lime $Ca(C_3H_5O_3)_2$. The formation of lactic acid from sugar becomes intelligible on comparing the formulæ—



1 molecule of cane-sugar, $C_{12}H_{22}O_{11}$
4 molecules of lactic acid, $C_{12}H_{24}O_{12}$.

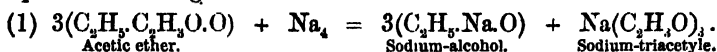
After a time the mass becomes more fluid, at the same time evolving bubbles of gas, which contain carbonic acid and hydrogen, for the lactate of lime is undergoing a fermentation, by which it is converted into butyrate of lime—



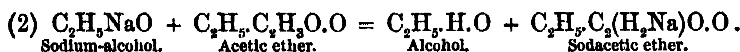
$$\underset{\text{Lactate of lime.}}{2Ca(C_3H_5O_3)_2} + H_2O = \underset{\text{Butyrate of lime.}}{Ca(C_4H_7O_2)_2} + CaO,CO_2 + 3CO_2 + H_8.$$

By distilling the butyrate of lime with dilute hydrochloric acid, an aqueous solution of butyric acid is obtained, and on saturating this with chloride of calcium, the acid collects as an oily layer upon the surface. It is remarkable for its powerful odour of rancid butter.*

Synthetical formation of acids of the acetic series.—By a very remarkable process of substitution, butyric acid has been derived from acetic acid. When sodium is heated with acetic ether, it is gradually dissolved, and the liquid solidifies on cooling, to a crystalline mass containing, among other products, *sodacetic ether*, or acetic ether in which one atom of the hydrogen has been displaced by sodium. The reaction appears to take place in two stages—



$$(1)\ \underset{\text{Acetic ether.}}{3(C_2H_5.C_2H_3O.O)} + Na_4 = \underset{\text{Sodium-alcohol.}}{3(C_2H_5.Na.O)} + \underset{\text{Sodium-triacetyle.}}{Na(C_2H_3O)_3}.$$



$$(2)\ \underset{\text{Sodium-alcohol.}}{C_2H_5NaO} + \underset{\text{Acetic ether.}}{C_2H_5.C_2H_3O.O} = \underset{\text{Alcohol.}}{C_2H_5.H.O} + \underset{\text{Sodacetic ether.}}{C_2H_5.C_2(H_2Na)O.O}.$$

By digesting the sodacetic ether with iodide of ethyl for several hours in a close vessel, at 212° F., the atom of sodium is exchanged for ethyle, and *ethacetic ether*, or butyric ether, is produced—



$$\underset{\text{Sodacetic ether.}}{C_2H_5.C_2(H_2Na)O_2} + \underset{\text{Iodide of ethyl.}}{C_2H_5I} = NaI + \underset{\text{Ethacetic or butyric ether.}}{C_2H_5.C_2H_2(C_2H_5)O_2}.$$

From this ether the ethacetic acid, $C_2H_3(C_2H_5)O_2$, has been prepared and found to be identical with butyric acid, $C_4H_8O_2$.

The connection thus established between butyric acid and the ethyle series helps to explain the production of that acid in the fermentation of sugar.

But butyric ether has also been obtained by another process of substitution, which affords a proof that the same substance may be correctly represented by two distinct rational formulæ.

The substitution of sodium for hydrogen in acetic ether may extend to two atoms of hydrogen, and if the *disodacetic ether* so produced be digested with iodide of methyle, butyric ether is obtained—

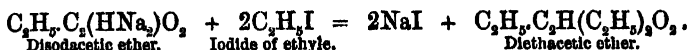


$$\underset{\text{Disodacetic ether.}}{C_2H_5.C_2(HNa_2)O_2} + \underset{\text{Iodide of methyle.}}{2CH_3I} = 2NaI + \underset{\text{Dimethacetic or butyric ether.}}{C_2H_5.C_2H(CH_3)_2O_2}.$$

* Butyric acid and some of its homologues (as valerianic and caproic) appear to be present in the perspiration of the skin, and to cause the disagreeable odour of close rooms.

So that butyric acid may be regarded, according to the method by which it is produced, either as ethacetic acid, formed from acetic acid by the substitution of an equivalent of ethyle for one of hydrogen, or as dimethacetic acid, resulting from the substitution of two equivalents of methyle for two of hydrogen.

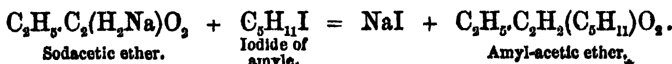
When disodacetic ether is acted on by iodide of ethyle, it yields diethacetic ether—



$$\underset{\text{Disodacetic ether.}}{C_2H_5.C_2(HNa_2)O_2} + \underset{\text{Iodide of ethyle.}}{2C_2H_5I} = 2NaI + \underset{\text{Diethacetic ether.}}{C_2H_5.C_2H(C_2H_5)_2O_2}.$$

This ether has an odour resembling peppermint, and its composition is the same as that of caproic ether, $C_2H_5.C_6H_{11}O_2$; but the *diethacetic acid* prepared from it, though isomeric with caproic acid ($C_6H_{12}O_2$), is not identical with it.

The acid next in the series, œnanthic ($HC_7H_{13}O_2$), may be obtained from the ether produced by the action of iodide of amyle upon sodacetic ether—

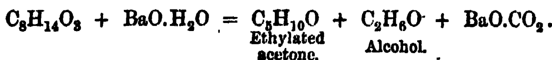


$$\underset{\text{Sodacetic ether.}}{C_2H_5.C_2(H_2Na)O_2} + \underset{\text{Iodide of amyle.}}{C_5H_{11}I} = NaI + \underset{\text{Amyl-acetic ether.}}{C_2H_5.C_2H_2(C_5H_{11})O_2}.$$

From this ether, the amyl-acetic acid, $H.C_2H_2(C_5H_{11})O_2$, which appears to be identical with œnanthic acid, has been obtained.

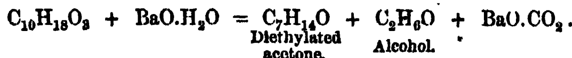
These reactions help to explain the production of several of the alcohols corresponding to the acetic series of acids, during the fermentation of grape husks (marc of the wine-press).

Among the products of the action of sodium and ethylic iodide upon acetic ether, is a liquid having the composition $C_8H_{14}O_3$, which, when distilled with alkaline bases, yields *ethylated acetone*, $C_3H_5(C_2H_5)O$, isomeric with the acetone of propionic acid (propione, $C_5H_{10}O$)—



$$C_8H_{14}O_3 + BaO.H_2O = \underset{\text{Ethylated acetone.}}{C_5H_{10}O} + \underset{\text{Alcohol.}}{C_2H_6O} + BaO.CO_2.$$

Another liquid produced by the action of ethylic iodide upon disodacetic ether has the composition $C_{10}H_{18}O_3$, which furnishes *diethylated acetone*, $C_3H_4(C_2H_5)_2O$, when distilled with baryta water—



$$C_{10}H_{18}O_3 + BaO.H_2O = \underset{\text{Diethylated acetone.}}{C_7H_{14}O} + \underset{\text{Alcohol.}}{C_2H_6O} + BaO.CO_2.$$

Diethylated acetone is a liquid smelling of camphor, and boiling at 280° F. It is isomeric with butyrone, which boils at 290° F., and with œnanthic aldehyde or œnanthole, which boils at 312° F.

By treating acetic ether with sodium and methylic iodide, the corresponding methylated acetones may be obtained.

Methylated acetone, $C_3H_5(CH_3)O$, has the odour of chloroform, and is identical with the ethyl-acetyle, $C_2H_3O.C_2H_5$, obtained by the action of zinc-ethyle upon chloride of acetyle.

Dimethylated acetone, $C_3H_4(CH_3)_2O$, has an odour of parsley.

Valerianic acid ($H.C_5H_9O_2$) derives interest from the circumstance that some of its salts, particularly the valerianate of zinc, are used medicinally.

This acid is found in valerian root, and in the berries of the guelder-rose. It is one cause of the peculiar odour of decaying cheese, and of whale and seal oils.

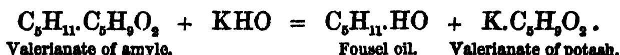
Artificially, it is best obtained by distilling fousel oil (amylic alcohol, $C_5H_{12}O$) with sulphuric acid and bichromate of potash, when the oxygen

of the chromic acid converts part of the amylic alcohol into valerianic acid—



$$C_5H_{12}O \text{ (Fousel oil)} + O_2 = C_5H_{10}O_2 \text{ (Valerianic acid)} + H_2O.$$

The distilled liquid is really a mixture of valerianic acid and valerianate of amyle ($C_5H_{11}.C_5H_9O_2$), but when treated with caustic potash, the latter is decomposed, yielding fousel oil and valerianate of potash.



$$\underset{\text{Valerianate of amyle.}}{C_5H_{11}.C_5H_9O_2} + KHO = \underset{\text{Fousel oil.}}{C_5H_{11}.HO} + \underset{\text{Valerianate of potash.}}{K.C_5H_9O_2}.$$

By distilling the valerianate of potash with sulphuric acid, the valerianic acid is obtained as an oily liquid of very remarkable odour, which recalls that of butyric acid.

406. The separation of the volatile acids belonging to the acetic series is a problem which frequently presents itself to the chemist, and is effected by a very instructive process of *partial saturation*, founded upon the principle, that when a mixture containing two acids with different boiling points is partially neutralised by an alkali and distilled, the more volatile of the two acids (*i.e.*, that having the lower boiling point) will pass over, whilst the other remains in combination with the alkali.

In applying this method, for example, to a mixture of valerianic acid (boiling at 347° F.) and butyric acid (boiling at 315° F.), in unknown proportions, the liquid would be divided into two equal parts, one of which would be exactly neutralised with potash, and then distilled together with the other half. If there were just enough valerianic acid to combine with the potash, pure valerianate of potash would be left in the retort, and the more volatile butyric acid would pass over. If there were more valerianic acid than would be required to combine with the potash, the excess of that acid would distil over, together with the butyric acid, whilst valerianate of potash alone would be left in the retort. By distilling this salt with sulphuric acid, the pure valerianic acid would be obtained, and the separation of the rest of the valerianic from the butyric acid would be effected by one or two repetitions of the process.

If the valerianic acid present in the mixture were not in sufficient quantity to combine with the potash added, then butyrate of potash, as well as valerianate, would be left in the retort, and pure butyric acid would distil over. By distilling the mixture of valerianate and butyrate of potash with sulphuric acid, a mixture of the two acids would be obtained which would require a repetition of the process.

In any case, it will be observed that this process must yield one of the acids in a state of purity.

The same principle applies to the separation of three or more volatile acids, but the process involves, of course, a greater number of distillations.

407. Soap.—The manufacture of soap affords an excellent instance of a process which was in use for centuries before anything was known of the principles upon which it is based, for it was not till the researches of Chevreul were published, in 1813, that any definite ideas were entertained with respect to the composition of the various fats and oils from which soaps are made.

The investigations of Chevreul are conspicuous among the labours which have contributed in so striking a manner to the rapid advancement of chemistry during the present century; undertaken when the chemistry

of organic substances had scarcely advanced beyond the dignity of an art, when the principles of classification were almost entirely empirical, and hardly any research had been published which could serve as a model, these researches reflect the remarkable sagacity and accuracy of their author.

The sense of our obligation to this eminent chemist is further increased, when we remember that the ultimate analysis of organic substances was then effected by a very difficult and laborious process, whilst the doctrine of combining proportions was so imperfectly understood, that it could afford but little assistance in confirming or interpreting the results of analysis.

All soaps result from the action of the alkalies upon the oils and fats.

In the manufacture of soap, potash and soda are the only alkalies employed, the former for soft, the latter for hard soaps.

The fatty matters employed by the soap-maker are chiefly tallow, palm oil, cocoa-nut oil, and kitchen stuff, for hard soaps, and seal oil and whale oil for soft soaps.

In the manufacture of hard soap, the alkali is prepared by boiling a solution of carbonate of soda (soda-ash) with lime to remove the carbonic acid—



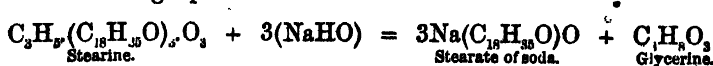
$$Na_2O.CO_2 + CaO.H_2O = CaO.CO_2 + Na_2O.H_2O \text{ (or } 2NaHO),$$

the clear solution of hydrate of soda, or *soda-ley*, being drawn off from the insoluble carbonate of lime.

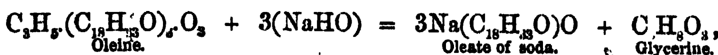
The tallow is at first boiled with a weak soda-ley, because the soap which is formed is insoluble in a strong alkaline solution, and would envelope and protect a quantity of undecomposed tallow; in proportion as the saponification proceeds, stronger leys are added, until the whole of the grease has disappeared. In order to separate the soap which is dissolved, advantage is taken of the insolubility of soap in solution of salt; a quantity of common salt being thrown into the boiler, the soap rises to the surface, when the *spent ley* is drawn off from below, and the soap transferred to iron moulds that it may harden sufficiently to be cut up into bars.

In order to understand the chemistry of this process, it is necessary to know that tallow is a mixture of two fatty substances, one of which, *stearine** ($C_{57}H_{110}O_6$), is solid, and the other, *oleine* ($C_{57}H_{104}O_6$), liquid, the quantity of stearine being about thrice that of oleine.

When these fats are acted upon by soda, they undergo decomposition, furnishing stearic and oleic acids, which combine with the soda to form soap, whilst a peculiar sweet substance, termed *glycerine*, passes into solution; the nature of the decomposition in each case will be understood from the following equations:—



$$\underset{\text{Stearine.}}{C_3H_5.(C_{18}H_{35}O)_3.O_3} + 3(NaHO) = \underset{\text{Stearate of soda.}}{3Na(C_{18}H_{35}O)O} + \underset{\text{Glycerine.}}{C_3H_8O_3}$$



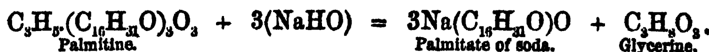
$$\underset{\text{Oleine.}}{C_3H_5.(C_{18}H_{33}O)_3.O_3} + 3(NaHO) = \underset{\text{Oleate of soda.}}{3Na(C_{18}H_{33}O)O} + \underset{\text{Glycerine.}}{C_3H_8O_3},$$

so that the soap obtained by boiling tallow with soda is a mixture of the stearate of soda with about a third of its weight of oleate of soda, and from 20 to 30 per cent of water.

Palm oil is composed chiefly of *palmitine* ($C_{51}H_{98}O_6$), a solid fat which

* Στέαρ, tallow.

is resolved by boiling with soda into palmitate of soda (palm oil soap) and glycerine—



$$C_3H_5.(C_{16}H_{31}O)_3O_3 + 3(NaHO) = 3Na(C_{16}H_{31}O)O + C_3H_8O_3.$$

Palmitine. Palmitate of soda. Glycerine.

In the fish oils, the predominant constituent is oleine, so that when boiled with hydrate of potash, they yield oleate of potash ($KC_{18}H_{33}O_2$), which composes the chief part of soft soap.

Castile soap is made from olive oil, which contains oleine and a solid fat known as *margarine.* The latter appears to be really composed of palmitine and stearine, so that the Castile soap is a mixture of oleate, palmitate, and stearate of soda.

The peculiar appearance of mottled soap is caused by the irregular distribution of a compound of the fatty acid with oxide of iron, which arranges itself in veins throughout the mass. If the soap contained too much water, so as to render it very fluid when transferred to the moulds, this iron compound would settle down to the bottom, leaving the soap clear, so that the mottled appearance is often regarded as an indication that the soap does not contain an undue proportion of water; it is imitated, however, by stirring into the pasty soap some sulphate of iron and a little impure ley containing sulphide of sodium, so as to produce the dark sulphide of iron by double decomposition.*

In the manufacture of yellow soap, in addition to tallow and palm oil, a considerable proportion of common rosin (see p. 465) is added to the soap shortly before it is finished.

Soft soap is not separated from the water by salt like hard soap, but is evaporated to the required consistency.

Transparent soaps are obtained by drying hard soap, dissolving it in hot spirit of wine, and pouring the strong solution into moulds after the greater part of the spirit has been distilled off.

Silicated soap is a mixture of soap with silicate of soda.

Glycerine soap is prepared by heating the fat with alkali and a little water to about 400° F. for two or three hours, and running the mass at once into moulds. It is, of course, a mixture of soap and glycerine.

The proportion of water in soaps is very variable, some specimens containing between 70 and 80 per cent. The smallest proportion is about 30 per cent.

The theory of saponification, stated above, has received the strongest confirmation within the last few years, by the synthetic production of the fats from glycerine and the fatty acids formed in their saponification.

Preparation of the fatty acids.—All the soaps, when mixed with acids, undergo decomposition, their alkalies combining with the acid added, whilst the fatty acids separate either in the solid form (in the case of stearic and palmitic acids), or as an oily liquid (in the case of oleic acid). Thus, if soap obtained by boiling tallow with soda be dissolved in hot water, and mixed with an excess of tartaric acid, an oil rises to the surface which concretes into a buttery mass on cooling. This mass, composed of stearic and oleic acids, is submitted to pressure in order to separate the greater part of the liquid oleic acid, and the stearic acid which is left is purified by crystallisation, first from alcohol, and afterwards from ether.

Stearic acid is thus obtained in transparent colourless plates which have

* A soap which contains much more than 30 per cent. of water is said not to admit of mottling.

the composition $HC_{18}H_{35}O_2$; they are, of course, insoluble in water, but dissolve in hot alcohol, the solution being acid to test-papers.

All the stearates are insoluble in water except those of the alkalies, so that if a solution of common soap (containing stearate of soda) be mixed with a solution of lime or magnesia, a stearate of lime or magnesia is separated in the insoluble form, and it will be remembered that this decomposition of soap is produced by the action of hard waters (page 44).

408. CANDLES.—Since tallow fuses at about 100° F., and stearic acid not below 159°, it is evident that, independently of other considerations, the latter would be better adapted for the manufacture of candles, for such candles would never soften at the ordinary atmospheric temperature in any climate, and would have much less tendency to *gutter* in consequence of the excessive fusion of the fuel around the base of the wick. The gases furnished by the destructive distillation of stearic acid in the wick of the candle burn with a brighter flame than those produced from tallow. Accordingly the manufacture of stearine (or more correctly, stearic acid) candles* has now become a very important and instructive branch of industry.

The original method of separating the stearic acid from tallow on the large scale, consisted in mixing melted tallow with lime and water, and heating the mixture for some time to 212° by passing steam through it. The tallow was thus converted into the insoluble stearate and oleate of lime, which was drained from the solution containing the glycerine, and decomposed by sulphuric acid. The mixture of stearic and oleic acids thus obtained was cast into thin slabs, which were packed between pieces of cocoa-nut matting, and well squeezed in a hydraulic press, which forced out the oleic acid, leaving the stearic and palmitic acids in a fit state for the manufacture of candles.

The separation of the solid fatty acids from tallow and other fats may also be effected by the action of sulphuric acid, a process extensively applied in this country to palm and cocoa-nut oils. These fats are mixed in copper boilers with about one-sixth of their weight of concentrated sulphuric acid, and heated by steam to about 350° F. for some hours, when part of the glycerine is converted into sulphoglyceric acid ($C_3H_8O_3.SO_3$), and the remainder is decomposed by the sulphuric acid, carbonic and sulphurous acids being disengaged, whilst a dark-coloured mixture of palmitic, stearic, and oleic acids is left. A part of the oleic acid becomes converted in this process into *elaidic acid*, which has the same composition, but differs from oleic acid in fusing at about 113° F., so that the amount of solid acid obtained by this process is much increased. This mixture is well washed from the adhering sulphuric and sulphoglyceric acids, and transferred to a copper still into which a current of steam is passed, which has been raised to about 600° F. by passing through hot iron pipes. These fatty acids could not be distilled alone without decomposition, but under the influence of a current of steam they pass over readily enough, leaving a black pitchy residue in the retort, which is employed in making black sealing-wax, and for other useful purposes.

The distilled fatty acids are broken up and pressed between cocoa-nut matting to remove the oleic acid.

One great advantage of this process, which is commonly, though incorrectly, styled the *saponification by sulphuric acid*, is its allowing the con-

* *Composite candles* are made of a mixture of stearic and palmitic acids

version of the worst kinds of refuse fat into a form fit for the manufacture of candles; thus the fat extracted from bones in the manufacture of glue, and that removed from wool in the scouring process, may be turned to profitable account.

It will be remarked that in this process the palmitic, stearic, and oleic acids are formed from the palmitine, stearine, and oleine existing in the fats, by the assimilation of the elements of water and the subsequent separation of glycerine, just as in the ordinary process of saponification by means of alkalies.

Strictly speaking, the action appears to consist of two stages; for when concentrated sulphuric acid is allowed to act upon the natural fats in the cold, it combines with each of their ingredients, forming the acids known as sulphostearic, sulphopalmitic, sulpholeic, and sulphoglyceric, which are soluble in water, though not (with the exception of the last) in water containing sulphuric acid.

The second stage consists in the decomposition of the sulpho-fatty acids by the high temperature in contact with steam, the sulphoglyceric acid having been in great measure decomposed into secondary products before the distillation is commenced.

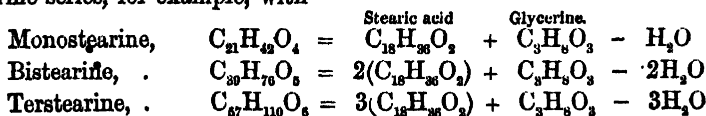
Within the last few years, the extraction of the solid acids from the natural fats has been effected by a process known as *saponification by steam*, which allows the glycerine also to be obtained in a pure state. It is only necessary to subject the fat, in a distillatory apparatus, to the action of steam, at a temperature of about 600° F., to cause both the fatty acids and the glycerine to distil over; the former may be separated as usual into solid and liquid portions by pressure, whilst the glycerine, which is obtained in aqueous solution below the layer of fatty acids, is concentrated by evaporation and sent into commerce as a very sweet colourless viscid liquid. The saponification of palmitine, for instance, by steam, would be represented by the equation—



$$\underset{\text{Palmitine.}}{C_3H_5.(C_{16}H_{31}O_2)_3} + 3H_2O = \underset{\text{Palmitic acid.}}{3(H.C_{16}H_{31}O_2)} + \underset{\text{Glycerine.}}{C_3H_8O_3}.$$

409. In the artificial formation of natural fats, this change has been reversed, for by heating 3 molecules of stearic, palmitic, or oleic acid with 1 molecule of glycerine, in a sealed tube, for several hours, to about 500° F., 3 molecules of water are eliminated, and stearine, palmitine, or oleine is produced.

By a similar process, compounds have been formed from glycerine with one and two molecules of the fatty acids, so that we are acquainted, in the stearine series, for example, with—



		Stearic acid	Glycerine.	
Monostearine,	$C_{21}H_{42}O_4$ =	$C_{18}H_{36}O_2$ +	$C_3H_8O_3$ −	H_2O
Bistearine, .	$C_{39}H_{76}O_5$ =	$2(C_{18}H_{36}O_2)$ +	$C_3H_8O_3$ −	$2H_2O$
Terstearine, .	$C_{57}H_{110}O_6$ =	$3(C_{18}H_{36}O_2)$ +	$C_3H_8O_3$ −	$3H_2O$

The last representing stearine as it exists in the natural fats.

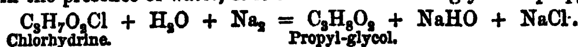
Nor is it only with the fatty acids, properly so called, that glycerine will furnish *glycerides*, as these bodies are termed, similar compounds having been obtained with acetic and benzoic acids.

The hydrogen-acids are also capable of acting upon glycerine in a similar manner. Thus, when glycerine ($C_3H_8O_3$) is acted on by hydrochloric acid, an oily liquid, *chlorhydrine* ($C_3H_7O_2Cl$), is obtained, the glycerine having combined with 1 molecule of hydrochloric acid, and 1 molecule of water having been separated.

Dichlorhydrine ($C_3H_6OCl_2$) results from the union of glycerine with 2 molecules of

hydrochloric acid, and separation of 2 molecules of water; whilst, to form *trichlorhydrine* ($C_3H_5Cl_3$), 3 molecules of hydrochloric acid are taken up, and 3 molecules of water removed.

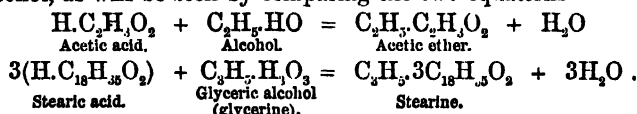
By the action of oxide of silver, in presence of water, the chlorhydrines may be reconverted into glycerine. The examination of these chlorhydrines has pointed out the method of effecting the conversion of a triatomic alcohol (glycerine) into a diatomic alcohol (glycol), for if chlorhydrine be acted on by sodium dissolved in mercury, in the presence of water, it is converted into the glycol of propylene—



$$\underset{\text{Chlorhydrine.}}{C_3H_7O_2Cl} + H_2O + Na_2 = \underset{\text{Propyl-glycol.}}{C_3H_8O_2} + NaHO + NaCl.$$

This tendency of glycerine to form compounds with the acids, the formation of which is attended (like that of the ethers from alcohol) with separation of the elements of water, has led chemists to look upon glycerine as an alcohol—a view which is also supported by its combining with sulphuric and phosphoric acids to form *sulphoglyceric* ($C_3H_8O_3.SO_3$) and *phosphoglyceric* acids, just as alcohol forms sulphovinic and phosphovinic acids. A compound has even been obtained, which is believed to stand to glycerine in a relation similar to that which ether bears to alcohol; the formula of this *glyceric ether*, as it is called, is $C_6H_{10}O_3$, differing from 2 molecules of glycerine ($C_6H_{16}O_6$) by the elements of 3 molecules of water.

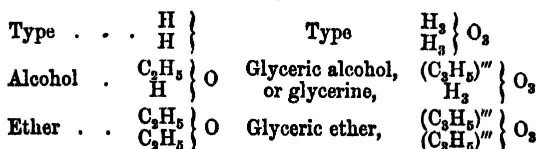
The formation of stearine from stearic acid and glycerine would then be quite analogous to that of acetic ether, for example, from acetic acid and alcohol, as will be seen by comparing the two equations—



$$\underset{\text{Acetic acid.}}{H.C_2H_3O_2} + \underset{\text{Alcohol.}}{C_2H_5.HO} = \underset{\text{Acetic ether.}}{C_2H_5.C_2H_3O_2} + H_2O$$

$$\underset{\text{Stearic acid.}}{3(H.C_{18}H_{35}O_2)} + \underset{\text{Glyceric alcohol (glycerine).}}{C_3H_5.H_3O_3} = \underset{\text{Stearine.}}{C_3H_5.3C_{18}H_{35}O_2} + 3H_2O.$$

The only difference between the two reactions is, that in the latter, 3 molecules of acid are concerned, and 3 molecules of water are formed. This circumstance, taken together with some other features of glycerine, has induced those chemists who consider alcohol as formed upon the type of a molecule of water, to look upon glycerine as derived in a similar manner from 3 molecules of water, in which half the hydrogen is replaced by the triatomic radical, *glyceryle* $(C_3H_5)'''$; thus—



Type . . .	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	Type	$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$
Alcohol .	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	Glyceric alcohol, or glycerine,	$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$
Ether . .	$\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$	Glyceric ether,	$\left.\begin{matrix}(C_3H_5)'''\\(C_3H_5)'''\end{matrix}\right\}O_3$

410. Glycerine is obtained on the small scale by boiling olive oil with litharge and water, until the stearic, oleic, and palmitic acids are converted into their lead-salts (*lead plaster*), which are insoluble, whilst the glycerine, together with a little oxide of lead, passes into solution. The lead is precipitated by hydrosulphuric acid, and the filtered liquid concentrated by evaporation.

The chief uses of glycerine as an application to the skin, and a remedy in cases of deafness, depend upon its oily consistency, and its want of volatility, which preserves surfaces to which it is applied in a moist and supple condition.

Glycerine cannot be distilled alone without decomposition, though it has been seen to be capable of distillation in a current of highly heated steam. When decomposed by distillation, it evolves very irritating vapours of *acroleine* (C_3H_4O), which is a constant product of the destructive distilla-

tion of fats containing glycerine, and gives rise to the peculiar disgusting odour of a smouldering tallow candle; *composite candles*, being made of stearic and palmitic acids (without glycerine) do not emit this odour of acroleine when blown out.

Acroleine is best obtained in the pure state by distilling glycerine with anhydrous phosphoric acid, which removes 2 molecules of water ($C_3H_8O_3 - 2H_2O = C_3H_4O$). It is a colourless liquid, distinguished by its intensely irritating vapour, which affects the eyes very strongly. From a chemical point of view it is interesting, as being the aldehyde of the allyle series (see p. 474), and, therefore, another link connecting that series with glycerine. By treatment with oxide of silver, acroleine is converted into *acrylic acid* ($C_3H_4O_2$), bearing the same relation to acroleine (C_3H_4O) that acetic acid ($C_2H_4O_2$) bears to ordinary aldehyde (C_2H_4O). The iodide of allyle and allylic alcohol have been already noticed (p. 474).

The allyle series, therefore, is perfectly parallel with the ethyle series, and it seems very probable that allylic alcohol is a member of a homologous series of alcohols having the general formula $C_nH_{2n}O$, with a series of acids corresponding to the acetic series, but having the general formula $C_nH_{2n-2}O_2$, of which the following members are known :—

Acrylic Series of Acids.

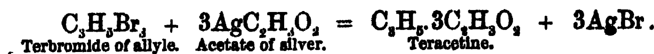
Acid.	Formula.	Source.
Acrylic . .	$C_3H_4O_2$	Oxidation of acroleine.
Crotonic .	$C_4H_6O_2$	Croton-seed oil.
Angelic . .	$C_5H_8O_2$	Angelica root.
Pyroterebic	$C_6H_{10}O_2$	Turpentine.
Damaluric .	$C_7H_{12}O_2$	Cow's urine (δάμαλις, *a calf*).
Campholic .	$C_{10}H_{18}O_2$	Camphor.
Moringic .	$C_{15}H_{28}O_2$	*Moringa aptera* (oil of ben).
Hypogæic .	$C_{16}H_{30}O_2$	Oil of ground nut.
Physetoleic		Sperm-whale oil (*Physeter macrocephalus*).
Oleic . .	$C_{18}H_{34}O_2$	Most oils.
Doeglic . .	$C_{19}H_{36}O_2$	Doegling train oil.
Brassic . .	$C_{22}H_{42}O_2$	Mustard seed (fixed) oil.
Erucic . .		Colza oil (*Brassica oleifera*).

These acids are monobasic, their salts being formed by the substitution of 1 equivalent of a metal for 1 of hydrogen.

The following table exhibits the principal members of the allyle series, together with the corresponding members of the ethyle series :—

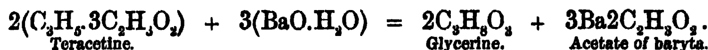
Ethyle Series.		*Allyle Series.*	
Ethyle, . . .	$C_2H_5.C_2H_5$	Allyle, . .	$C_3H_5.C_3H_5$
Ether, . . .	$(C_2H_5)_2O$	Allylic ether, .	$(C_3H_5)_2O$
Alcohol, . .	$C_2H_5.HO$	Allylic alcohol,	$C_3H_5.HO$
Iodide of ethyle, .	C_2H_5I	Iodide of allyle,	C_3H_5I
Acetic ether, .	$C_2H_5.C_2H_3O_2$	Acetate of allyle,	$C_3H_5.C_2H_3O_2$
Aldehyde, . .	C_2H_4O	Allyle aldehyde,	C_3H_4O (acroleine)
Acetic acid, . .	$C_2H_4O_2$	Acrylic acid, .	$C_3H_4O_2$
Sulphide of ethyle,	$(C_2H_5)_2S$	Sulphide of allyle,	$(C_3H_5)_2S$ (oil of garlic)
Triethylamine, .	$N(C_2H_5)_3$	Triallylamine, .	$N(C_3H_5)_3$
Hydrate of tetrethylium, . .	$N(C_2H_5)_4.HO$	Hydrate of tetrallylium, .	$N(C_3H_5)_4.HO$.

It has been seen (p. 474) that glycerine, when distilled with biniodide of phosphorus, yields iodide of allyle (C_3H_5I). When this liquid is treated with bromine it yields a crystallisable *terbromide of allyle*, $C_3H_5Br_3$; and if this be decomposed by acetate of silver, it furnishes the glyceride known as *teracetine*, thus—



$$\underset{\text{Terbromide of allyle.}}{C_3H_5Br_3} + \underset{\text{Acetate of silver.}}{3AgC_2H_3O_2} = \underset{\text{Teracetine.}}{C_3H_5.3C_2H_3O_2} + 3AgBr.$$

When teracetine is submitted to the action of hydrate of baryta, glycerine is reproduced—

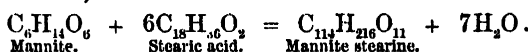


$$\underset{\text{Teracetine.}}{2(C_3H_5.3C_2H_3O_2)} + 3(BaO.H_2O) = \underset{\text{Glycerine.}}{2C_3H_8O_3} + \underset{\text{Acetate of baryta.}}{3Ba2C_2H_3O_2}.$$

This affords an interesting example of the conversion of a monatomic radical, allyle $(C_3H_5)'$, into a triatomic radical, glyceryle $(C_3H_5)'''$.

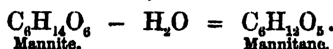
411. A very interesting chemical similarity has been pointed out between glycerine and mannite ($C_6H_{14}O_6$). It will be remembered that the former is a constant product of the alcoholic fermentation, and the latter, of a peculiar kind of fermentation (the viscous), to which saccharine liquids are subject.

When mannite is heated, under pressure, with the acids of the acetic series, it forms compounds corresponding to those obtained when glycerine is so treated. Thus, with stearic acid—



$$\underset{\text{Mannite.}}{C_6H_{14}O_6} + \underset{\text{Stearic acid.}}{6C_{18}H_{36}O_2} = \underset{\text{Mannite stearine.}}{C_{114}H_{216}O_{11}} + 7H_2O.$$

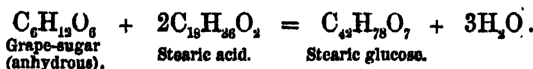
But it will be observed that 7 molecules of water are here eliminated instead of 3, as in the case of glycerine. The further examination of mannite explains this, for it is not that substance which is the true analogue of glycerine, but one which is obtained by heating mannite to 400° F., when it loses a molecule of water, and is converted into *mannitane*—



$$\underset{\text{Mannite.}}{C_6H_{14}O_6} - H_2O = \underset{\text{Mannitane.}}{C_6H_{12}O_5}.$$

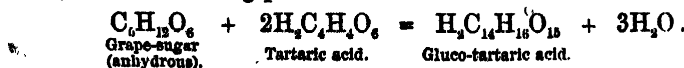
This mannitane or mannite-glycerine is a viscous substance, presenting a very strong resemblance to glycerine, so that it is not unlikely to have been mistaken for this substance in examining some of the natural fats. The *mannite-glycerides*, or compounds formed by heating mannite with the fatty acids, are scarcely to be distinguished from stearine, palmitine, &c. They are saponified by alkalies in exactly the same manner.

Cane-sugar and grape-sugar are capable of forming compounds corresponding to those obtained by the action of acids upon glycerine and mannite. Thus, if grape-sugar be heated to 250° F. for several hours in contact with stearic acid, it is converted into a fusible solid, insoluble in water, but soluble in alcohol and ether—



$$\underset{\text{Grape-sugar (anhydrous).}}{C_6H_{12}O_6} + \underset{\text{Stearic acid.}}{2C_{18}H_{36}O_2} = \underset{\text{Stearic glucose.}}{C_{42}H_{78}O_7} + 3H_2O.$$

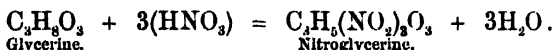
When grape-sugar is heated with tartaric acid, a similar reaction takes place, but the resulting product is a new acid—



$$\underset{\text{Grape-sugar (anhydrous).}}{C_6H_{12}O_6} + \underset{\text{Tartaric acid.}}{2H_2C_4H_4O_6} = \underset{\text{Gluco-tartaric acid.}}{H_2C_{14}H_{16}O_{15}} + 3H_2O.$$

Cane-sugar behaves in a similar manner.

412. *Nitroglycerine*, or *glonoine*.—This violently explosive substance is very easily prepared by dissolving glycerine in a mixture of equal measures of the strongest nitric and sulphuric acids, previously cooled, and pouring the solution in a thin stream into a large volume of water, when the nitroglycerine is precipitated as a colourless heavy oil (sp. gr. 1·6). It is advisable to add the glycerine to the mixed acids in very small quantities at a time, and to cool the mixture in a vessel of water after each addition. When the nitroglycerine has subsided, the water may be poured off, and the oil shaken several times with water, so as to wash it thoroughly. The formation of nitroglycerine resembles that of gun-cotton (see p. 497), three atoms of hydrogen being removed from the glycerine by the oxidising action of the nitric acid, and three of nitric peroxide introduced in their place—



$$\underset{\text{Glycerine.}}{C_3H_8O_3} + 3(HNO_3) = \underset{\text{Nitroglycerine.}}{C_3H_5(NO_2)_3O_3} + 3H_2O.$$

On a larger scale, a mixture of concentrated nitric acid (sp. gr. 1·47 to 1·49) with twice its weight of concentrated sulphuric acid is employed. The mixture is placed in stone jars containing about 7 lbs. each, which are immersed in running water, and about 1 lb. of glycerine (sp. gr. 1·25) is gradually added, with frequent stirring, to the contents of each jar, care being taken that the temperature does not rise above 80° F. The mixture is allowed to settle for a quarter of an hour, and poured gradually into 5 or 6 gallons of water. The oily nitroglycerine which falls to the bottom is well washed by stirring with water, a little alkali being added in the last washings. One per cent. of magnesia is sometimes added to the nitroglycerine in order to neutralise any acid arising from decomposition.

This oil is very violent in its explosive effects. If a drop of nitroglycerine be placed on an anvil and struck sharply, it explodes with a very loud report, even though not free from water; and if a piece of paper moistened with a drop of it be struck, it is blown into small fragments. On the application of a flame or of a red-hot iron to nitroglycerine, it burns quietly; and when heated over a lamp in the open air it explodes but feebly. In a closed vessel, however, it explodes at about 360° F. with great violence. For blasting rocks, the nitroglycerine is poured into a hole in the rock, *tamped* by filling the hole with water, and exploded by the concussion caused by a detonating fuse (see p. 500). It has been stated to produce the same effect in blasting as ten times its weight of gunpowder, and much damage has occurred from the accidental explosion of nitroglycerine in course of transport. When nitroglycerine is kept, especially if it be not thoroughly washed, it decomposes, with evolution of nitrous fumes and formation of crystals of oxalic acid; and it may be readily imagined that, should the accumulation of gaseous products of decomposition burst one of the bottles in a case of nitroglycerine, the concussion would explode the whole quantity.

Nitroglycerine is particularly well fitted for blasting, because it will explode with equal violence whether moisture be present or not. On the other hand, it is very poisonous, and is said to affect the system seriously by absorption through the skin, and the gases resulting from its explosion are exceedingly acrid. Again, its fluidity prevents its use in any but downward bore-holes. To overcome these objections, and to diminish the danger of transport, several blasting compounds have been proposed, of which nitroglycerine is the basis.

Dynamite is composed of a particularly porous siliceous earth, obtained from Oberlohe in Hanover, impregnated with about 70 per cent. of nitroglycerine.

Glyoxyline is a name given to gun-cotton pulp and saltpetre mixed with nitroglycerine. *Lithofracteur* is a more complex mixture containing about half its weight of nitroglycerine, together with nitrate of soda, sulphur, powdered coal, sawdust, and siliceous earth. *Dualine* is composed of nitroglycerine and sawdust.

Nitroglycerine is readily soluble in ether and in wood-naphtha, but somewhat less so in alcohol; it is reprecipitated by water from these last solutions. It becomes solid at 40° F., a circumstance which is unfavourable to its use in mining operations, partly because it is then less susceptible of explosion by the detonating fuze, and partly because serious accidents are said to have resulted from attempts to thaw the frozen nitroglycerine by heat, or to break it up with tools. It is remarkable that when made on the small scale, the nitroglycerine may generally be cooled down to 0° F. without becoming hard. This and other observations render it probable that some other substitution product is occasionally mixed with it.

OILS AND FATS.

413. A very remarkable feature in the history of the fats is the close resemblance in chemical composition and properties which exists between them, whether derived from the vegetable or the animal kingdom. They all contain two or more neutral substances which furnish glycerine when saponified, together with some of the acids of the acetic series or of series closely allied to it.

One of the most useful vegetable fatty matters is *palm-oil*, which is extracted by boiling water from the crushed fruit of the *Elais guineensis*, an African palm. It is a semi-solid fat, which becomes more solid when kept, since it then undergoes a species of fermentation, excited apparently by an albuminous substance contained in it, in consequence of which the palmitine ($C_{51}H_{98}O_6$) is converted into glycerine and palmitic acid. The bleaching of palm-oil is effected by the action of a mixture of sulphuric or hydrochloric acid and bichromate of potash, which oxidises the yellow colouring matter.

Cocoa-nut oil is also semi-solid, and is remarkable for the number of acids of the acetic series which it yields when saponified, viz., caproic, caprylic, rutic, lauric, myristic, and palmitic.

These fats are chiefly used in the manufacture of soap and candles.

Salad oil, or *sweet oil* (olive oil), is obtained by crushing olives, and an inferior kind which is used for soap is obtained by boiling the crushed fruit with water. When exposed to a temperature of about 32° F. a considerable portion of the oil solidifies; this solid portion is generally called *margarine* ($C_{54}H_{104}O_6$); it is much less soluble in alcohol than stearine, though more so than palmitine. When saponified, margarine yields glycerine and *margaric acid* ($C_{17}H_{34}O_2$). This acid appears to be really composed of stearic and palmitic acids, into which it may be separated by repeated crystallisation from alcohol, when the palmitic acid is left in solution. The fusing-point of margaric acid is 140° F., that of stearic being 159°, and that of palmitic, 144°, but a mixture of 10 parts of palmitic with 1 part of stearic acid fuses at 140°.

That portion of the olive oil which remains liquid below 32° consists of *oleine* ($C_{57}H_{104}O_6$), and forms nearly three-fourths of its weight. Oleine is not so easily saponified as the solid fats, and is resolved by

that process into glycerine and oleic acid ($C_{18}H_{34}O_2$), which differs from the other fatty acids by remaining liquid at temperatures above 40° F., and by absorbing oxygen from the air, when it is converted into a new acid which is not solidified by cold.

Oleic acid is used in greasing wool for spinning, being much more easily removed by alkalies than olive oil which was formerly employed. Oleate of ammonia is sometimes employed as a mordant for the aniline dyes on cotton.

The characteristic feature of oleic acid is its furnishing a solid crystallised acid when submitted to destructive distillation; this acid is called *sebacic acid*, and is one of a series of dibasic acids, most of the other members of which may be obtained from oleic acid by the action of nitric acid.

Dibasic Fatty Acid Series.

Acid.	Formula.	Source.
Oxalic .	$C_2H_2O_4$	*Oxalis acetosella* (wood sorrel), &c.
Malonic .	$C_3H_4O_4$	Oxidation of malic acid.
Succinic .	$C_4H_6O_4$	Amber (*succinum*).
Lipic	$C_5H_8O_4$	Oxidation of oleic acid (λίπος, *fat*).
Adipic .	$C_6H_{10}O_4$	,, ,, (*adeps fat*),
Pimelic .	$C_7H_{12}O_4$	,, ,, (πῖμελή, *fat*).
Suberic .	$C_8H_{14}O_4$	Oxidation of stearic acid, and of cork (*suber*).
Anchoic* . Lepargylic†	$C_9H_{16}O_4$	Oxidation of Chinese wax, and of cocoa-nut oil.
Sebacic .	$C_{10}H_{18}O_4$	Distillation of oleic acid.

The neutral salts of the acids of this series are formed by the displacement of two atoms of hydrogen by a metal. Thus, neutral succinate of potash has the composition $C_4(H_4K_2)O_4$.

It is worthy of remark, that nine acids of the series, $C_nH_{2n}O_2$ (from acetic to capric inclusive), are found among the products of the action of nitric acid upon oleic acid.

It is well known that salad oil becomes rancid, and exhales a disagreeable odour after being kept for some time. This appears to be due to a fermentation similar to that noticed in the case of palm oil, originally started by the action of atmospheric oxygen upon albuminous matters present in the oil; the neutral fatty matters are thus partly decomposed, as in saponification, their corresponding acids being liberated, and giving rise (in the case of the higher members of the acetic series, such as caproic and valerianic) to the disagreeble odour of rancid oil. By boiling the altered oil with water, and afterwards washing it with a weak solution of soda, it may be rendered sweet again.

Almond oil, extracted by a process similar to that employed for olive oil, is also very similar in composition; but *colza oil*, obtained from the seeds of the *Brassica oleifera*, contains only half its weight of oleine, and hence solidifies more readily than the others.

Colza oil is largely used for burning in lamps, and undergoes a process of purification from the mucilaginous substances which are extracted with

* From ἄγχω, *to throttle*, from its suffocating vapours.
† From λέπαργος, *having white skin*.

it from the seed, and leave a bulky carbonaceous residue when subjected to destructive distillation in the wick of the lamp. To remove these, the oil is agitated with about 2 per cent. of oil of vitriol, which carbonises the mucilaginous substances, but leaves the oil untouched. When the carbonaceous flocks have subsided, the oil is drawn off, washed to remove the acid, and filtered through charcoal.

Linseed oil, obtained from the seeds of the flax plant, is much richer in oleine than any of the foregoing, exhibiting no solidification till cooled to 15° or 20° F. below the freezing point. It exhibits, however, in a far higher degree, a tendency to become solid when exposed to the air, which has acquired for it the name of a *drying oil*, and renders it of the greatest use to painters. This solidification is attended with absorption of oxygen, which takes place so rapidly in the case of linseed oil, that spontaneous combustion has been known to take place in masses of rag or tow which have been smeared with it.*

The tendency of linseed oil to solidify by exposure is much increased by heating it with about $\frac{1}{20}$th of litharge, or $\frac{1}{10}$th of binoxide of manganese; these oxides are technically known as *dryers*, and oil so treated is called *boiled linseed oil*. The action of these metallic oxides is not well understood.

The strong drying tendency of linseed oil is supposed to be due to a peculiarity in the oleine, which is said not to be ordinary oleine, but to furnish a different acid, *linoleic acid*, when saponified. When linseed oil is exposed for some time to a high temperature, it becomes viscous and treacly, and is used in this state for the preparation of printing-ink. If the viscous oil be boiled with dilute nitric acid, it is converted into *artificial caoutchouc*, which is used in the manufacture of surgical instruments. This property appears to be connected with the drying qualities of the oil.

Castor oil, obtained from the seeds of *Ricinus communis*, also yields a peculiar acid when saponified, termed *ricinoleic* ($H.C_{18}H_{33}O_3$), containing one more atom of oxygen than oleic acid, which it much resembles. The destructive distillation of castor oil yields *œnanthic acid* ($H.C_7H_{13}O_2$), and *œnanthole* or *œnanthic aldehyde* ($C_7H_{14}O$), and by distilling it with caustic potash, caprylic alcohol ($C_8H_{18}O$) is obtained. As in the case of olive oil, the *cold drawn* castor oil, which is expressed from the seeds without the aid of heat, is much less liable to become rancid. Castor oil is much more soluble in alcohol than any other of the fixed oils.

The various *fish oils*, such as seal and whale oil, also consist chiefly of oleine, and appear to owe their disagreeable odour to the presence of certain volatile acids, such as valerianic.

Cod-liver oil appears to contain, in addition to oleine and stearine, a small quantity of *acetine* ($C_9H_{14}O_6$), which yields acetic acid and glycerine when saponified. Some of the constituents of bile have also been traced in it, as well as minute quantities of iodine and bromine.

Butter contains about two-thirds of its weight of solid fat, which consists in great part of margarine (see p. 574), but contains also *butine*, which yields glycerine and *butic acid* ($H.C_{20}H_{39}O_2$) when saponified. The liquid portion consists chiefly of oleine. Butter also contains small quantites of butyrine, caproine, and caprine, which yield, when saponified, glycerine and butyric ($H.C_4H_7O_2$), caproic ($H.C_6H_{11}O_2$), and capric ($H.C_{10}H_{19}O_2$) acids, distinguished for their disagreeable odour.

* During the oxidation, a volatile compound is formed which resembles acroleine in smell, and colours unsized paper brown. It has been suggested that the brown colour and musty smell of old books may be due to the oxidation of the oil in the printing-ink.

Fresh butter has very little odour, being free from these volatile acids, but if kept for some time, especially if the caseine of the milk has been imperfectly separated in its preparation, spontaneous resolution of these fats into glycerine and the volatile disagreeable acids takes place. By salting the butter this change is in great measure prevented.

The fat of the sheep and ox (*suet*, or when melted, *tallow*), consists chiefly of stearine, whilst in that of the pig (*lard*) oleine predominates to about the same extent as in butter. Margarine (or palmitine ?) is also present in these fats. *Benzoated lard* contains some gum benzoin, which prevents it from becoming rancid.

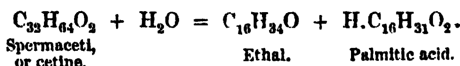
Human fat contains chiefly oleine and margarine (or, if we do not admit the independent existence of the latter, palmitine and stearine).

Sperm oil, which is expressed from the spermaceti found in the brain of the sperm whale, owes its peculiar odour to the presence of a fat which has been called *phocenine*, but which appears to be *valerine*, as it yields glycerine and valerianic acid ($H.C_5H_9O_2$) when saponified.

The beautiful solid crystalline fat, known as *spermaceti* or *cetine*, differs widely from the ordinary fatty matters, for when saponified (which is not easily effected), it yields no glycerine, but in its stead another alcohol termed *ethal* ($C_{16}H_{34}O$), which is a white crystalline solid, capable of being distilled without decomposition.

The soap prepared from spermaceti, when decomposed by an acid, yields palmitic acid ($H.C_{16}H_{31}O_2$), (formerly called *ethalic acid*), to which ethal is the corresponding alcohol.

Palmitic acid and ethal are formed from spermaceti by the assimilation of the elements of water, just as stearic acid and glycerine are formed from stearine—



$$\underset{\text{Spermaceti, or cetine.}}{C_{32}H_{64}O_2} + H_2O = \underset{\text{Ethal.}}{C_{16}H_{34}O} + \underset{\text{Palmitic acid.}}{H.C_{16}H_{31}O_2}.$$

Upon the compound radical theory, ethal would be represented as cetylic hydrate ($C_{16}H_{33}$)HO, and as the alcohol of the cetyle series, running parallel with the ethyle series. The following characteristic members of the series have been studied :—

Cetyle Series.		*Ethyle Series.*	
Cetylene,	$C_{16}H_{32}$	Ethylene,	C_2H_4
Cetylic ether,	$(C_{16}H_{33})_2O$	Ether,	$(C_2H_5)_2O$
Ethal,	$C_{16}H_{33}.HO$	Alcohol,	$C_2H_5.HO$
Palmitic acid,	$C_{16}H_{31}O_2.H$	Acetic acid,	$C_2H_3O_2.H$
Spermaceti,	$C_{16}H_{33}.C_{16}H_{31}O_2$	Acetic ether,	$C_2H_5.C_2H_3O_2$

Chinese wax, the produce of an insect of the cochineal tribe, is analogous in its chemical constitution to spermaceti. When saponified by fusion with caustic potash, it yields *cerotine* or *cerylic alcohol* ($C_{27}H_{55}.HO$), corresponding to ethal, and *cerotic acid* ($H.C_{27}H_{53}O_2$), corresponding to palmitic acid. Cerotic acid is also contained in ordinary bees' wax, from which it may be extracted by boiling alcohol, and crystallises as the solution cools. It forms about two-thirds of the weight of the wax. Cerotic acid is found among the products of oxidation of paraffine by chromic acid.

Bees' wax also contains about one-third of its weight of *myricine* ($C_{46}H_{92}O_2$), a substance analogous to spermaceti, which yields, when saponified, palmitic acid and *melissine* ($C_{30}H_{61}.HO$), an alcohol corresponding to ethal. The colour, odour, and tenacity of bees' wax appear to be due

to the presence of a greasy substance called *ceroleine*, which forms about $\frac{1}{20}$th of the wax, and has not been fully examined. The *tree wax* of Japan is said to be pure palmitine.

Wax is bleached for the manufacture of candles, by exposing it in thin strips or ribands to the oxidising action of the atmosphere, or by boiling it with nitrate of soda and sulphuric acid. Chlorine also bleaches it, but displaces a portion of the hydrogen in the wax, taking its place and causing the evolution of hydrochloric acid vapours when the wax is burnt.

The following table includes the principal fatty bodies and their corresponding acids, with their fusing points :—

Neutral Fats.	Formula.	Chief Source.	Fusing Point.	Fatty Acids.	Formula.	Fusing Point.
Stearine*	$C_{57}H_{110}O_6$	Tallow	125° to 157°	Stearic	$C_{18}H_{36}O_2$	159°
Palmitine	$C_{51}H_{98}O_6$	Palm oil	114° to 145°	Palmitic	$C_{16}H_{32}O_2$	144°
Margarine	$C_{54}H_{104}O_6$	Olive oil	116°	Margaric	$C_{17}H_{34}O_2$	140°
Oleine	$C_{57}H_{104}O_6$	"	Below 32°	Oleic	$C_{18}H_{34}O_2$	40°
Cetine	$C_{32}H_{64}O_2$	Spermacceti	120°	Palmitic	$C_{16}H_{32}O_2$	144°
Myricine	$C_{46}H_{92}O_2$	Bees' wax	162°	"		

VEGETABLE ACIDS.

414. *Oxalic acid.*—This very poisonous acid occurs pretty abundantly in the vegetable kingdom, being found in the leaves of the wood sorrel as binoxalate of potash (*salt of sorrel*, KHC_2O_4.Aq.), in the stalks of rhubarb, in some sea-weeds, as oxalate of soda, and in lichens, some of which contain more than half their weight of oxalate of lime. Oxalate of lime has also been found in wood. In certain unhealthy conditions of the animal frame, oxalate of lime is produced, being either excreted in the urine, or forming a calculus (*mulberry calculus*) in the bladder. In such cases the oxalic acid appears to be formed in consequence of an imperfection in that oxidising process by which the carbon and hydrogen of the various parts of the frame are finally converted into carbonic acid (CO_2) and water (H_2O), the production of oxalic acid ($C_2H_2O_4$) representing the penultimate stage of that process.

Guano contains a considerable quantity of oxalic acid in combination with ammonia and lime.

With the exception of carbonic acid, no carbon compound is more commonly met with than oxalic acid, as a product of the action of oxidising agents upon organic substances, especially upon those which do not contain nitrogen, such as sugar ($C_{12}H_{22}O_{11}$), starch ($C_6H_{10}O_5$), and woody fibre.

Oxalic acid is largely employed in calico-printing, in cleansing leather and brass, as a solvent for Prussian blue in the preparation of blue ink, &c., and for taking iron-mould out of linen. It is manufactured on the large scale by oxidising sawdust with a mixture of hydrate of potash and hydrate of soda; the latter would not produce oxalic acid without the hydrate of potash, and this alone would be too expensive. 1 mol. of

* Stearine and palmitine are said to present three modifications with different fusing points. Some recent observations appear to indicate that the so-called palmitine of palm oil really contains stearine, oleine, and laurine

hydrate of potash and 2 mols. of hydrate of soda are mixed in solution, which should have the sp. gr. 1·35, made into a thick paste with sawdust, and heated upon iron plates for several hours; hydrogen is evolved, from the decomposition of the water in the alkaline hydrates, the oxygen serving to convert the wood into oxalic acid, which forms more than one-fourth of the weight of the grey mass finally obtained. On treating this mass with cold water, a quantity of oxalate of soda is left undissolved; this is boiled with hydrate of lime, when the oxalic acid is converted into the insoluble oxalate of lime, and hydrate of soda is dissolved; the oxalate of lime is then decomposed by dilute sulphuric acid, when the sparingly soluble sulphate of lime is formed, and the solution yields crystals of oxalic acid ($H_2C_2O_4.2Aq.$) on evaporation. The whole of the alkali originally employed is recovered by evaporating the liquors to dryness, calcining to destroy organic matter, and decomposing the alkaline carbonates with hydrate of lime. The sawdust yields about half its weight of crystallised oxalic acid.

Before the introduction of this process, oxalic acid was sold at nearly twice its present cost, being then usually obtained by the action of nitric acid either upon molasses or upon starch-sugar* (p. 490) in leaden vessels, which were found to remain unattacked by the acid as long as any sugar remained unoxidised.

For experiment on the small scale, oxalic acid may be prepared by gently heating 100 grains of starch with 1¼ measured ounce of nitric acid (sp. gr. 1·38), when abundant fumes of nitrous acid (N_2O_3) will indicate the deoxidation suffered by the nitric acid. When this has abated, the solution may be transferred to a dish, and slowly evaporated to about one-sixth of its bulk; on cooling, a mass of beautiful four-sided prismatic crystals of oxalic acid will be obtained.

The crystals of oxalic acid may be represented by the empirical formula $C_2H_6O_6$, but when they are heated to 212° F. they lose water, melting first, if the heat be suddenly applied,† but efflorescing without fusion if heated gradually. The dried or effloresced oxalic acid has the composition $C_2H_2O_4$, showing that 2 mols. of water of crystallisation have been expelled, and that the crystals would be more correctly represented by $C_2H_2O_4.2Aq.$ On neutralising oxalic acid with potash and soda, salts are obtained which, when dried at 212° F., have the composition $K_2C_2O_4$, and $Na_2C_2O_4$, and if solutions of these salts be precipitated by nitrate of lead or of silver, the oxalates of lead (PbC_2O_4) and of silver ($Ag_2C_2O_4$) are obtained. If the dried acid be heated to about 320° F., it sublimes in crystals, but above that temperature it is decomposed into water, carbonic acid, carbonic oxide, and some formic acid (see p. 557). When heated with dehydrating agents, such as sulphuric acid, it is also decomposed into carbonic acid and carbonic oxide (p. 86).

Oxalic acid is rather sparingly soluble in cold water, requiring about nine times its weight; hot water dissolves it more abundantly, and it is moderately soluble in alcohol. The aqueous solution is intensely acid, more nearly resembling the strong mineral acids than one of vegetable origin, and is exceedingly poisonous, a property which is the more dangerous on account of the resemblance of the crystallised oxalic acid to Epsom salts (sulphate of magnesia), from which, however, it may be readily distinguished by its sour taste and by the action of heat, which

* Hence the common name, *acid of sugar*.

† By suddenly heating the crystals with a lamp in a test-tube, much of the acid may be sublimed in long prismatic crystals.

entirely dissipates the oxalic acid, but only expels water from Epsom salts. Fortunately, a considerable quantity of the acid is required to cause death, in ordinary cases 100 grains or more. The chemical antidote employed to counteract its effect is chalk suspended in water, the lime of the chalk combining with the acid to form the insoluble and harmless oxalate of lime ($CaO.C_2O_3$). The insolubility of the oxalate of lime renders the oxalic acid one of the most delicate tests for lime, which may be detected, for example, in common water, by adding oxalic acid and a slight excess of ammonia, when a white cloud of oxalate of lime is produced. Conversely, of course, salts containing calcium (chloride of calcium, for instance) may be employed to detect oxalic acid, the precipitated oxalate of lime being distinguished from other similar precipitates by its insolubility in acetic acid.

As might be expected from its composition ($C_2H_2O_4$), oxalic acid is easily converted into carbonic acid and water by oxidising agents; thus, if a hot solution of oxalic acid be poured upon powdered binoxide of manganese, violent effervescence takes place from the rapid evolution of carbonic acid.

Binoxalate of potash ($KHC_2O_4.H_2O$) is sold under the names of *salt of sorrel* and *essential salt of lemons*, and is employed for the same purposes as oxalic acid. It is a sparingly soluble salt, requiring 40 parts of cold water to dissolve it, and has occasionally caused accidents by being mistaken for cream of tartar (bitartrate of potash), from which it is readily distinguished by the action of heat, which chars the bitartrate, but not the binoxalate, an alkaline mass containing carbonate of potash being left in both cases.

Quadroxalate of potash ($KH_3 2C_2O_4.2H_2O$) is also sometimes sold as salts of lemon; it is even less soluble than the binoxalate.

Oxalate of ammonia ($(NH_4)_2C_2O_4.H_2O$), so much used in chemical analysis as a precipitant for lime, is obtained by mixing solution of oxalic acid with a slight excess of ammonia, and evaporating the solution, from which the oxalate of ammonia crystallises, on cooling, in fine prismatic needles.

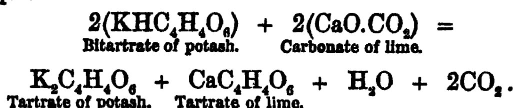
The action of heat upon this salt has been described at p. 540.

Oxalate of silver ($Ag_2C_2O_4$) is obtained as a white precipitate when nitrate of silver is added to oxalate of ammonia. It is remarkable for being decomposed, with a slight explosion, when heated in the dry state, metallic silver being left, $Ag_2C_2O_4 = Ag_2 + 2CO_2$.

415. *Tartaric acid.*—The most important of the vegetable acids is tartaric acid ($C_4H_6O_6$) which occurs in many fruits, but more especially in the grape, the juice of which deposits it, during fermentation, in the form of bitartrate of potash, which is known in commerce as *tartar* or *argol.* This salt dissolves with difficulty in cold water, but may be dissolved in boiling water, from which it crystallises in prisms on cooling. When thus purified, it is known as *cream of tartar*, and has the composition $KHC_4H_4O_6$, representing tartaric acid in which one atom of hydrogen has been replaced by potassium. The solution of this salt is acid to test-papers, and if it be neutralised with potash and evaporated, it yields crystals of a very soluble salt, having the composition $K_2C_4H_4O_6$. This is the neutral tartrate of potash, cream of tartar being a bitartrate. The crystallised tartaric acid is therefore regarded as $H_2C_4H_4O_6$.

In order to prepare tartaric acid, which is largely used in dyeing and

calico-printing, the impure bitartrate of potash is boiled with water, and carbonate of lime (chalk) is added as long as it causes effervescence from the escape of carbonic acid; the result of this change is the formation of tartrate of lime, which is insoluble, and tartrate of potash, which dissolves in the water—



$$\underset{\text{Bitartrate of potash.}}{2(KHC_4H_4O_6)} + \underset{\text{Carbonate of lime.}}{2(CaO.CO_2)} =$$

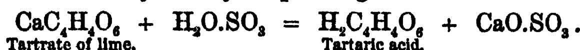
$$\underset{\text{Tartrate of potash.}}{K_2C_4H_4O_6} + \underset{\text{Tartrate of lime.}}{CaC_4H_4O_6} + H_2O + 2CO_2.$$

Chloride of calcium is then added to the mixture, which converts the whole of the tartaric acid into the insoluble tartrate of lime—



$$K_2C_4H_4O_6 + CaCl_2 = 2KCl + CaC_4H_4O_6.$$

The tartrate of lime is strained off, washed, and boiled with diluted sulphuric acid, when sulphate of lime remains undissolved, and tartaric acid may be obtained in crystals by evaporating the filtered solution—

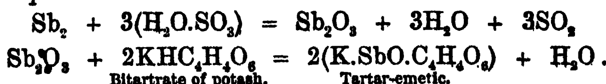


$$\underset{\text{Tartrate of lime.}}{CaC_4H_4O_6} + H_2O.SO_3 = \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} + CaO.SO_3.$$

Large transparent prisms are thus obtained, which are soluble in about three-fourths of their weight of hot water. When kept, the solution, unless very strong, deposits a curious fungoid growth,* and acetic acid is found in it. When heated to about 340° F., the crystals fuse without loss of weight; but on examining the fused mass, it is found to be no longer tartaric acid, but a mixture of two new acids. One of these, *metatartaric acid*, has the same formula as tartaric acid ($H_2C_4H_4O_6$), but cannot be crystallised. Its salts are more soluble in water than the tartrates, and are converted into the latter when boiled with water. The other acid, *isotartaric*, is also uncrystallisable, but has the formula ($HC_4H_5O_6$). The isotartrate of potash ($KC_4H_5O_6$) has the same composition as the bitartrate ($KHC_4H_4O_6$), but is far more soluble. It is converted into that salt by boiling with water.

At 374° F. tartaric acid loses water, and is converted into *tartaric anhydride* ($C_8H_8O_{10}$), which is a white insoluble substance, convertible into tartaric acid by prolonged contact with water.

Tartar-emetic.—One of the commonest salts of tartaric acid is *tartar-emetic*, the double tartrate of antimony and potash, which is prepared by boiling antimony with sulphuric acid, driving off the excess of acid by heat, and digesting the residual teroxide of antimony with cream of tartar and a little water for some hours. The changes involved in the process are thus represented—



$$Sb_2 + 3(H_2O.SO_3) = Sb_2O_3 + 3H_2O + 3SO_2$$

$$Sb_2O_3 + \underset{\text{Bitartrate of potash.}}{2KHC_4H_4O_6} = \underset{\text{Tartar-emetic.}}{2(K.SbO.C_4H_4O_6)} + H_2O.$$

On boiling the mixture with water, and filtering, the cooled solution deposits octahedral crystals, of the formula $2(K.SbO.C_4H_4O_6),Aq$.

The water of crystallisation may be expelled at 212° F.; and if the salt be heated to 400° F. it loses an additional molecule of water, and becomes $K.Sb.C_4H_2O_6$, which is reconverted into tartar-emetic when dissolved in water.

When a little hydrochloric acid is added to a solution of tartar-emetic, a precipitate of teroxide of antimony is formed, which dissolves easily in an excess of the acid.

* This fungus has been found to contain 3·5 per cent. of nitrogen.

If kept for a length of time in solution, tartar-emetic is decomposed, octahedral crystals of teroxide of antimony being deposited, and the solution ceases to be precipitated by hydrochloric acid. The reaction to test-paper, which was slightly acid, is now slightly alkaline.

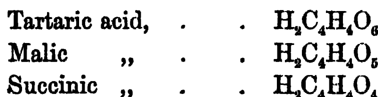
Compounds perfectly analogous to tartar-emetic have been obtained, in which the antimony is replaced by boron or by arsenic, and the potassium by silver, lead, or sodium.

It will be observed that tartar-emetic presents an anomaly in its composition, for it might be expected to be $KSb'''(C_4H_4O_6)_2$. The composition of the tartar-emetic, dried at 400° F., might be reconciled with that of crystallised tartaric acid by representing it thus, $C_4(H_2KSb''')O_6$, that is, crystallised tartaric acid ($C_4H_6O_6$), in which one atom of hydrogen has been replaced by potassium, and three atoms by the triatomic antimony.

The beautiful prismatic crystals known as *Rochelle salt* consist of a double tartrate of potash and soda ($KNaC_4H_4O_6$, 4Aq.), prepared by neutralising cream of tartar with carbonate of soda.

Tartaric acid has been obtained artificially by the action of nitric acid upon sugar of milk or gum, which supplies a link of connection between this acid and the members of the sugar group which accompany it in plants.

Tartaric acid is easily convertible into succinic and malic acids, as might be anticipated from an inspection of their formulæ—



Tartaric acid, . .	$H_2C_4H_4O_6$
Malic " . .	$H_2C_4H_4O_5$
Succinic " . .	$H_2C_4H_4O_4$

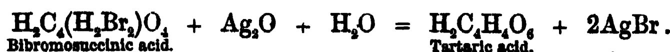
When tartaric acid is heated with phosphorus and iodine in the presence of water (or, which amounts to the same thing, when it is heated with hydriodic acid), the acid is deoxidised, and malic and succinic acids are produced, thus—



$$\underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} + 4HI = \underset{\text{Succinic acid.}}{H_2C_4H_4O_4} + I_4 + 2H_2O.$$

Tartaric and malic acids are frequently associated in fruits, and succinic acid is found among the products of fermentation of grape-juice.

Succinic acid may be reconverted into tartaric acid by heating it with bromine and water, when it is converted into bibromosuccinic acid, $H_2C_4(H_2Br_2)O_4$, which furnishes tartaric acid when decomposed with oxide of silver—



$$\underset{\text{Bibromosuccinic acid.}}{H_2C_4(H_2Br_2)O_4} + Ag_2O + H_2O = \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} + 2AgBr.$$

When bromosuccinic acid, $H_2C_4(H_3Br)O_4$, is decomposed with oxide of silver, malic acid is formed—



$$\underset{\text{Bromosuccinic acid.}}{2H_2C_4(H_3Br)O_4} + 3Ag_2O = \underset{\text{Malate of silver.}}{2Ag_2C_4H_4O_5} + 2AgBr + H_2O.$$

416. The tartaric acid found in grapes is accompanied, particularly in those of certain vintages and districts, by another acid called *racemic* or *paratartaric* acid, which has the same composition as tartaric acid, but crystallises with a molecule of water ($H_2C_4H_4O_6$.Aq.) The crystalline forms of these acids are the same, but the crystals of racemic acid effloresce, from loss of water, when exposed to the air. Solution of racemic acid is precipitated by the salts of lime, which do not precipitate tartaric acid unless it be previously neutralised. Moreover, although racemic acid

forms, with potash and oxide of antimony, a salt corresponding in composition to tartar-emetic, this does not crystallise in octahedra, but in tufts of needles.

There is a marked difference in the action of these two acids and their salts upon polarised light, for solutions of racemic acid and the racemates do not alter the plane of polarisation, whilst tartaric acid and the tartrates rotate it to the right.

On carefully examining the crystalline forms of the tartrates, Pasteur observed that they generally presented an exception to that law of crystalline symmetry, which requires that a modification existing on any edge or face of a crystal should be repeated on all its other similar edges or faces, whereas in the crystals of the tartrates, certain of the edges are truncated without any corresponding modification of the others, and *hemihedral* forms are thus produced. Now, in general, it is found that if a substance forms hemihedral crystals, their hemihedrism is of such a character that they can be superposed upon each other, so that the united crystals shall exhibit a perfect symmetry upon each side of the plane of junction; but the hemihedrism of the tartrates is such, that the crystals do not exhibit this symmetry when superposed upon each other, but when one is superposed upon the reflection of the other in a mirror, so that instead of presenting crystals which are, as usual, partly right and partly left-handed in their want of symmetry, the crystals of the tartrates are either all right-handed or all left-handed hemihedral crystals.

When the action of solutions of these salts upon polarised light came to be examined, it was found that the right-handed crystals always rotated the plane of polarisation to the right, whilst the left-handed crystals produced a left-handed rotation.

On separating the acids from these salts, they resembled each other precisely in all their chemical properties, but the acid from the right-handed salts furnished crystals which were hemihedral right-handedly, whilst that of the left-handed salts furnished left-handed hemihedral crystals; moreover, the solution of the right-handed acid exerted a right-handed rotation upon the plane of polarisation, which was turned in the opposite direction by a solution of the left-handed acid.

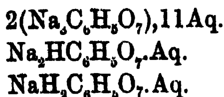
The former acid has been named dextro-tartaric acid, and is the usual form in which this acid is met with; the other acid has been called lævo-tartaric acid. In their chemical relations these acids are perfectly identical; for the chemist they are both the same tartaric acid, equally well adapted for all the uses to which this acid is applied.

Pasteur found that the double racemate of soda and ammonia furnished a crop of crystals containing both right-handed and left-handed hemihedral forms, and on separating them by hand, he found that the action of their solutions on polarised light corresponded with their hemihedrism, and on isolating the acids, the right-handed crystals furnished dextro-tartaric, the left-handed, lævo-tartaric acid.

This analysis of racemic acid was soon confirmed by its synthesis. On mixing concentrated solutions of equal parts of dextro-tartaric and lævo-tartaric acids, a considerable rise of temperature was observed, showing that combination had taken place, and the solution, which had no longer the power of rotating the plane of polarisation, furnished crystals of racemic acid.

This remarkable instance of chemical combination between two acids which are, in their chemical properties, perfectly identical, to furnish a new acid differing from both, affords, by analogy, some support to the theory of the *duplex* constitution of many elementary and compound bodies.

417. *Citric acid* ($C_6H_8O_7$) occurs in lemons, oranges, and most acidulous fruits. It is prepared from lemon-juice, which contains the acid in a free state, by neutralising it with chalk, when the citrate of lime ($Ca_3 2C_6H_5O_7$) is obtained, which is decomposed by dilute sulphuric acid; the filtered solution, when evaporated, yields prismatic crystals of citric acid, which contain $C_6H_8O_7.Aq$. They fuse at 212° F., and lose the water of crystallisation. From the formula of the citrate of lime, it will be seen that citric acid is tribasic, and should be written $H_3.C_6H_5O_7$; hence, like ordinary phosphoric acid, it forms three series of salts. The citrates of soda, for example, have the composition—



$$2(Na_3C_6H_5O_7),11Aq.$$
$$Na_2HC_6H_5O_7.Aq.$$
$$NaH_2C_6H_5O_7.Aq.$$

When citric acid is heated above 300° F., it is converted into *aconitic acid* ($H_3C_6H_3O_6$), another vegetable acid found in the different varieties of monkshood (*aconitum*).

Citric acid is employed in dyeing and calico-printing, as well as in medicine.

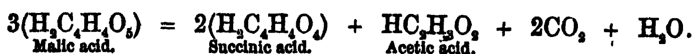
By fermentation in contact with yeast, the citrate of lime is converted into acetate and butyrate of lime, with evolution of carbonic acid and hydrogen. The crude citrate of lime prepared in Sicily, and imported for the preparation of the acid, is found sometimes to undergo this change spontaneously, so that it has been recommended to neutralise the hot lemon-juice with carbonate of magnesia (which is abundant in Italy), when the tribasic citrate of magnesia is precipitated in minute crystals. By dissolving this precipitate in a fresh quantity of hot lemon-juice, and evaporating, the bibasic citrate of magnesia is obtained in crystals, which is recommended as the best form in which to import the acid into this country.

418. *Malic acid* ($H_2C_4H_4O_5$) is a crystalline acid found, as its name implies, in apples, and in many other fruits. It is present, together with oxalic acid, in rhubarb. Tobacco leaves also contain it in the form of bimalate of lime, $CaH_22C_4H_4O_5$.

In order to extract the malic acid from rhubarb stalks, it is converted into malate of lime, the solubility of which enables it to be separated from the insoluble citrate and tartrate of lime. The juice is squeezed out of the stalks by a press, nearly neutralised with slaked lime suspended in water, and chloride of calcium is added. The precipitate containing tartrate, citrate, phosphate, and oxalate of lime, is filtered off, and the liquid boiled down, when malate of lime ($CaC_4H_4O_5$) is separated. This is washed and added to hot nitric acid, diluted with ten measures of water, as long as it continues to be dissolved. On cooling, bimalate of lime is deposited, which is dissolved in water and decomposed by acetate of lead, when it gives a curious precipitate of malate of lead ($PbC_4H_4O_5.3Aq.$), which becomes crystalline on standing, and fuses in the liquid below the temperature of boiling water. By suspending the malate of lead in water, and decomposing it with hydrosulphuric acid, the lead is separated as sulphide, and a solution of malic acid is obtained, which gives deliquescent prismatic crystals of the acid when evaporated to a syrup and set aside. Malic acid is decomposed by heat into two isomeric acids, the *malæic* and *fumaric* $H_2C_4H_2O_4$; the latter is found in the plant known as *fumitory* (*Fumaria officinalis*).

An excellent source of malic acid is the juice of the unripe berries of the mountain-ash, in which it is accompanied by a volatile oily acid of pungent aromatic odour; this has been called *parasorbic acid*, and has the formula $HC_6H_7O_2$. When fused with hydrate of potash, or boiled with a strong mineral acid, it suffers a remarkable conversion into a crystalline solid acid, having precisely the same composition, called *sorbic acid.*

Under the influence of yeast, in the presence of water, malate of lime is converted into succinate and acetate of lime—



$$\underset{\text{Malic acid.}}{3(H_2C_4H_4O_5)} = \underset{\text{Succinic acid.}}{2(H_2C_4H_4O_4)} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} + 2CO_2 + H_2O.$$

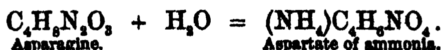
The amide of malic acid, *malamide*, $C_4H_8N_2O_3$ (malate of ammonia, $(NH_4)_2C_4H_4O_5$ *minus* $2H_2O$), has attracted some attention, because it has the same composition as *asparagine*, a crystalline substance extracted from the juice of asparagus, marsh-mallow root, and some other plants; but it is not identical with it, though asparagine, when acted on by nitrous acid, yields malic acid—



$$\underset{\text{Asparagine.}}{C_4H_8N_2O_3} + N_2O_3 = \underset{\text{Malic acid,}}{H_2C_4H_4O_5} + H_2O + N_4.$$

Asparagine is really the amide of another acid, the *aspartic*, into the

ammonia-salt of which it becomes converted when heated for some time with water—



$$C_4H_8N_2O_3 + H_2O = (NH_4)C_4H_6NO_4.$$

Asparagine. Aspartate of ammonia.

419. *Tannic acid*, or *tannin* ($C_{27}H_{22}O_{17}$) the astringent principle of gall-nuts, from which it may be extracted by water, is characterised by two very useful properties, viz., by yielding a black precipitate with the salts of peroxide of iron, and by forming a tough insoluble compound with gelatine and gelatigenous membrane, the first being turned to account in the preparation of ink, and the second in that of leather.

For the preparation of ink, three quarters of a pound of bruised nut-galls are digested in a gallon of cold water, and six ounces of green vitriol (sulphate of iron) are added, together with six ounces of gum, and a few drops of kreasote. The mixture is set aside for two or three weeks, being occasionally agitated, and the ink afterwards poured off from the undissolved part of the nut-galls.

Pure sulphate of iron ($FeO.SO_3$) and tannic acid might be mixed without change; but when the mixture is exposed to the air, oxygen is absorbed, converting the protoxide of iron (FeO) into sesquioxide (Fe_2O_3), which combines with the tannic acid to form a black precipitate of tannate of sesquioxide of iron, the exact composition of which is not known. The gum is added to render the liquid viscous, so as to prevent the subsidence of the black precipitate, and the kreasote prevents the ink from becoming mouldy. The brown colour of the ink in old manuscripts is due to the tannic acid having been partly removed by oxidation, leaving the brown peroxide of iron; the stain of *iron-mould* left by ink on linen after washing is due to the entire removal of the tannic acid by the alkali in the soap.

Tanning.—When infusion of nut-galls is added to a solution of gelatine, the latter combines with the tannic acid, and a bulky precipitate is obtained. If a piece of skin, which has the same composition as gelatine, be placed in the infusion of nut-galls, it will absorb the whole of the tannic acid, and become converted into leather, which is much tougher than the raw skin, less permeable by water, and not liable to putrefaction.

The first operation in the conversion of hides into leather, after they have been cleansed, consists in soaking them for three or four weeks in pits containing lime and water, which saponifies the fat, and loosens the hair. The same object is sometimes attained by allowing the hides to enter into putrefaction, when the resulting ammonia has the same effect as the lime. The loosened hair having been scraped off, the hides are soaked for twelve hours in water containing $\frac{1}{1000}$th of sulphuric acid, which removes adhering lime, and opens the pores of the skin, so as to fit it to receive the tanning liquid.

The tanning material generally employed for hides is the infusion of oak-bark, which contains *querci-tannic acid*, very similar in properties to tannic acid. The hides are soaked in an infusion of oak-bark for about six weeks, being passed in succession through several pits, in which the strength of the infusion is gradually increased. They are then packed in another pit with alternate layers of coarsely ground oak-bark; the pit is filled with water, and left at rest for three months, when the hides are transferred to another pit, and treated in the same way; but, of course, the position of the hides will be now reversed—that which was uppermost, and in contact with the weakest part of the tanning liquor, will now be

at the bottom. After the lapse of another three months the hide is generally found to be tanned throughout, a section appearing of a uniform brown colour. It has now increased in weight from 30 to 40 per cent. The chemical part of the process being now completed, the leather is subjected to certain mechanical operations to give it the desired texture. For tanning the thinner kinds of leather, such as morocco, a substance called *sumach* is used, which consists of the ground shoots of the *Rhus Coriaria*, and contains a large proportion of tannic acid.

Morocco leather is made from goat and sheep skins, which are denuded of hair by liming in the usual way, but the adhering lime is afterwards removed by means of a bath of sour bran or flour. In order to tan the skin so prepared, it is sewn up in the form of a bag, which is filled with infusion of sumach, and allowed to soak in a vat of the infusion for some hours. A repetition of the process, with a stronger infusion, is necessary; but the whole operation is completed in twenty-four hours. The skins are now washed and dyed, except in the case of red morocco, which is dyed before tanning, by steeping it first in alum or chloride of tin, as a mordant, and afterwards in infusion of cochineal. Black morocco is dyed with acetate of iron, which acts upon the tannic acid. The aniline dyes are now much employed for dyeing morocco.

The *kid* of which gloves are made is not actually tanned, but submitted to an elaborate operation called *tawing*, the chief chemical features of which are the removal of the excess of lime,* and opening the pores of the skin by means of a sour mixture of bran and water, in which lactic acid is the agent; and the subsequent impregnation of the porous skin with chloride of aluminum, by steeping it in a hot bath containing alum and common salt. The skins are afterwards softened by kneading in a mixture containing alum, flour, and the yolks of eggs. The putrefaction of the skin is as effectually prevented by the chloride of aluminum as by tanning.

Wash leather and *buckskin* are not tanned, but *shamoyed*, which consists in sprinkling the prepared skins with oil, folding them up and *stocking* them under heavy wooden hammers for two or three hours. When the grease has been well forced in, they are exposed in a warm atmosphere, to promote the drying of the oil by absorption of oxygen (p. 572). These processes having been repeated the requisite number of times, the excess of oil is removed by a weak alkaline bath, and the skins are dried and rolled. The buff colour of wash-leather is imparted by a weak infusion of sumach.

Parchment is made by stretching lamb or goat skin upon a frame, removing the hair by lime and scraping, as usual, and afterwards rubbing with pumice stone, until the proper thickness is acquired.

Tannic acid, like many other proximate constituents of vegetables (see p. 472), when boiled with diluted sulphuric acid, yields grape-sugar, whilst a new acid may be obtained from the solution, which is known as gallic acid†—



$$\underset{\text{Tannic acid.}}{C_{27}H_{22}O_{17}} + 5H_2O = \underset{\text{Gallic acid.}}{3(C_7H_6O_5)} + \underset{\text{Grape-sugar.}}{C_6H_{14}O_7}.$$

The addition of dilute sulphuric acid to the infusion of gall-nuts pro-

* Polysulphides of sodium and calcium are sometimes employed for removing the hair.

† It will be perceived that tannic acid is analogous in constitution to the gluco-tartaric acid mentioned at p. 568, which splits into grape-sugar and tartaric acid when boiled with diluted sulphuric acid, exactly as tannic acid splits into grape-sugar and gallic acid.

duces a precipitate composed of tannic and sulphuric acids, but this dissolves when boiled with excess of sulphuric acid, suffering the above change.

420. *Gallic acid* ($H_3C_7H_3O_5$) is also formed by the oxidation of tannic acid when exposed to the air, particularly in the presence of the matters associated with it in the gall-nut, which seem to act like the ferment in the quick vinegar process (p. 487). The method generally practised for obtaining gallic acid consists in exposing powdered nut-galls in a moist state to the action of the air for some weeks, in a warm place, when oxygen is absorbed, and carbonic acid evolved, the powder becoming covered with crystals of gallic acid (tannic acid does not crystallise). By boiling the mass with water, the gallic acid is extracted, and since, unlike tannic acid, it is very sparingly soluble in cold water, the greater portion crystallises out as the solution cools, in long silky needles, containing $C_7H_6O_5.Aq$.

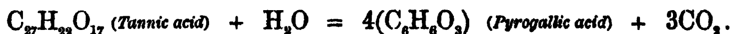
In this process another acid is obtained in small quantity, which is insoluble in water, and has been called *ellagic acid* ($HC_7H_2O_4$); it possesses some interest, because it is found as a product of animal life in certain intestinal concretions or *bezoars*, occurring in the antelopes of Central Asia.*

In most astringent substances a small quantity of gallic acid accompanies the tannic.

Gallic acid dissolves in oil of vitriol with a red colour, and when the solution is poured into water, a red-brown precipitate is obtained, called *rufigallic acid* ($C_7H_6O_5$), which is interesting from its property of dyeing calico red, if previously mordanted with alum.

When powdered nut-galls are heated in an iron pan surmounted with a cone of paper (see benzoic acid, p. 468) to about 420°, a quantity of crystals sublime into the cone, which are *pyrogallic acid* ($C_6H_6O_3$), or more properly, *pyrogalline*, for it is doubtful whether it is really an acid substance.

Its formation from the tannic acid of the galls is explained by the equation—



$$C_{27}H_{22}O_{17} \text{ (Tannic acid)} + H_2O = 4(C_6H_6O_3) \text{ (Pyrogallic acid)} + 3CO_2.$$

As its name implies, this acid may also be obtained by the action of heat upon gallic acid, which suffers a similar decomposition.†

This substance is extensively prepared for use in photography, in which art its great tendency to absorb oxygen is called into play, rendering it capable of decomposing the salts of silver with immediate separation of the metal.

The solution of pyrogallic acid soon becomes brown when exposed to the air, from absorption of oxygen, and if it be mixed with an alkali, it absorbs oxygen almost instantaneously, acquiring a very dark brown colour. This property renders pyrogallic acid very useful in the analysis of air and of other gases containing uncombined oxygen; a portion of air con-

* Ellagic acid is obtained as a crystalline precipitate by heating together, for some time, gallic and arsenic acids in solution;



$$\underset{\text{Gallic acid.}}{4(C_7H_6O_5)} + 2As_2O_5 = \underset{\text{Ellagic acid.}}{4(C_7H_3O_4)} + As_2O_3 + 6H_2O.$$

† By heating gallic acid under pressure with two or three parts of water to 410° F. for half-an-hour, and evaporating the solution, it is said that the theoretical quantity of pyrogallic acid may be obtained. It may be decolorised with animal charcoal.

fined in a graduated tube over mercury (see fig. 83), is shaken with a strong solution of potash to absorb carbonic acid, and the diminution of volume having been noted, some solution of pyrogallic acid in four parts of water is introduced; on shaking for a few seconds, the oxygen is entirely absorbed, when the volume of the nitrogen may be observed.

The salts of tannic and gallic acids are not very well known. The latter appears to be a tribasic acid, so that its true formula would be $H_3C_7H_3O_5$ the H_3 being replaceable by a metal.

The acid character of pyrogallic acid is very feeble.

The three acids are distinguished by their action upon the salts of iron. With pure protosulphate of iron ($FeO.SO_3$) neither tannic nor gallic acid gives any reaction, but pyrogallic acid gives a deep indigo blue solution; whilst with persulphate ($Fe_2O_3.3SO_3$) or perchloride (Fe_2Cl_6) of iron, the two former give a bluish-black precipitate, and pyrogallic acid gives a bright red solution.

The presence of tannic acid in a vegetable infusion is easily recognised by the addition of perchloride of iron, but the hue which is produced is not the same in all astringent substances, because they contain different varieties of *tannin.*

All these varieties, however, differ from tannic acid properly so called, in not furnishing pyrogallic acid when heated.

The astringent principle of *catechu* (*terra Japonica* or *cutch*) and *kino,* which are used by tanners and dyers, is called *mimotannic acid.*

VEGETABLE ALKALOIDS.

421. In some plants the vegetable acids are combined with vegetable alkalies or alkaloids; thus in opium, the morphine is combined with meconic acid; in cinchona bark, the quinine is combined with kinic acid. The methods adopted for the separation of these alkaloids from the acids and other substances associated with them are among the most important processes of practical chemistry.

Extraction of the alkaloids from opium.—Opium is the concrete milky juice which exudes on incising the unripe capsules of the *Papaver somniferum,* and is imported into this country from Persia, Turkey, Bengal, and Egypt, in the form of round masses or cakes enveloped in leaves; it has a dark colour, a soft waxy consistence, and a peculiar characteristic odour. Different samples vary much in composition, but the following result of an analysis of Smyrna opium will give an idea of the nature of this complex drug:—

100 *parts of Smyrna Opium contained*—

Gum,	26·2	Narcéine,	6·7
Caoutchouc,	6·0	Meconine,	0·8
Resin,	3·6	Codeine,	0·7
Oily matter,	2·2	Colouring and other organic matters,	19·1
Meconic acid,	5·0	Water,	9·9
Morphine,	10·8		
Narcotine,	6·8		

The medicinal value of opium appears to be due chiefly to the morphine ($C_{17}H_{19}NO_3$), which is present, for the most part, in the state of meconate of morphine; in order to obtain it in the separate state, the opium is cut into slices and digested with water at a moderate heat for two or three

hours; the liquor is then strained and evaporated, a little chalk being added to neutralise the free acid. The concentrated solution, containing chiefly morphine and codeine, in combination with meconic and sulphuric acids, is mixed with solution of chloride of calcium, when the meconic acid is precipitated in combination with lime, carrying with it a great part of the colouring matter, and leaving in solution the hydrochlorates of morphine and codeine, which may be obtained in crystals by evaporation. The hydrochlorates are decolorised with animal charcoal and recrystallised. On adding ammonia to the solution containing these salts, the morphine only is precipitated, and may be purified by crystallisation from alcohol, which deposits it in white rectangular prisms, having the formula $C_{17}H_{19}NO_3.Aq$.

The solution from which the morphine has been precipitated still contains the hydrochlorate of codeine, and on decomposing it with potash, the codeine is precipitated in crystals, of the composition $C_{18}H_{21}NO_3.Aq$.

The mother-liquor from the hydrochlorates of morphine and codeine contains narcotine, narcéine, meconine, thebaine, and papaverine, together with resin and colouring matter.*

The leading features of morphine are its sparing solubility in cold water, its bitter taste and alkaline reaction, and narcotic poisonous properties. It is generally identified by its giving an inky blue colour with perchloride of iron, and a golden yellow with nitric acid.

The *hydrochlorate of morphine* ($C_{17}H_{19}NO_3.HCl$), or *muriate of morphia*, is the chief form in which this alkaloid is used medicinally.

Narcotine ($C_{22}H_{23}NO_7$) possesses some interest as having been the first base extracted from opium, whence it may be obtained by simply treating the drug with ether, in which the morphine is insoluble. The greater part of the narcotine is left in the residue after exhausting the opium with water, from which it is extracted by digestion with acetic acid; on neutralising the solution with ammonia, narcotine is precipitated. It is a weak base, and has no alkaline reaction.

The *meconic acid* which exists in opium is a tribasic acid, having the formula $H_3C_7HO_7$; it is soluble in hot water, and crystallises on cooling in plates which contain three molecules of water of crystallisation. It gives a blood-red colour with solution of perchloride of iron.

422. *Extraction of quinine.*—The *cinchona* or *Peruvian bark*, so highly prized for its medicinal qualities, is obtained chiefly from the districts around the Andes, and is imported in three varieties, of which the yellow cinchona is richest in quinine, the pale or grey bark in cinchonine, whilst the red bark contains both these bases in considerable quantity. The alkaloids are combined with *kinic acid*, and with a variety of tannin known as quinotannic acid.

In order to extract them, the bruised bark is boiled with diluted hydrochloric acid, and the filtered solution, containing the hydrochlorates of quinine and cinchonine, is mixed with enough lime diffused through water to render it alkaline. The quinine and cinchonine, which are very sparingly soluble in cold water (requiring about 400 times their weight to dissolve them), are precipitated together with some of the colouring matter of the bark.

The precipitate having been collected upon a linen strainer and strongly pressed, is treated with boiling alcohol, which dissolves both the alkaloids,

* Κώδεια, *a poppy head*; *νάρκη*, torpor; *μήκων*, a poppy.

leaving any excess of lime undissolved. A part of the alcohol is then recovered by distillation, and the solution containing the quinine and cinchonine is neutralised with sulphuric acid, so as to convert the alkaloids into sulphates, and is then decolorised with animal charcoal, and allowed to crystallise. Sulphate of quinine, being much less soluble in water than the sulphate of cinchonine, crystallises out first, leaving the latter in solution.

The sulphate of quinine is dissolved in water and decomposed by ammonia, when the quinine is separated as a white powder, which may be dissolved in alcohol and crystallised.

The liquid from which the sulphate of quinine has been deposited contains, in addition to the sulphate of cinchonine, another base having the same composition as quinine, but distinguished from it by the indisposition of its sulphate to crystallise. This base is termed *quinidine*, and is produced from quinine under the influence of an excess of acid; it is the most important constituent of the substance called *quinoidine* or *amorphous quinine* which is prepared for sale from the mother-liquors of the sulphate of quinine, and forms a cheap substitute for quinine in medicine.

Quinine crystallises in small prisms, which have the composition $C_{20}H_{24}N_2O_2.3Aq.$, and although sparingly soluble, even in boiling water, it has an extremely bitter taste, which is also possessed by its salts.

Quinine is employed in medicine in the form of sulphate—



$$(C_{20}H_{24}N_2O_2)_2H_2O.SO_3.7Aq.)$$

which requires as much as 700 parts of cold water to dissolve it, but is readily dissolved in water acidulated with sulphuric acid, when it is converted into the acid sulphate of quinine ($C_{20}H_{24}N_2O_2.H_2O.SO_3$). The solution is remarkable for its action upon light, for although it is perfectly colourless when held directly in front of the eye, if seen obliquely it appears to have, especially at the edge, a beautiful pale blue colour. This phenomenon, which is termed *fluorescence*, has been already referred to in the case of other substances (p. 473).

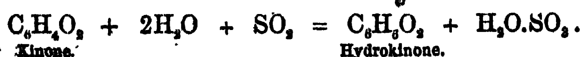
Quinic or *kinic acid.*—By evaporating the infusion of cinchona bark from which the quinine and cinchonine have been separated by lime, crystals of kinate of lime are obtained, and by decomposing these with sulphuric acid, the *kinic acid* ($HC_7H_{11}O_6$) passes into solution, whence it may be obtained in prismatic crystals.

This acid is chiefly interesting on account of the peculiar properties of some of its derivatives. When distilled with sulphuric acid and binoxide of manganese, the oxygen evolved from the mixture converts the kinic acid into a new substance, which condenses in beautiful yellow needles called *kinone* or *quinone*—



$$\underset{\text{Kinic acid.}}{HC_7H_{11}O_6} + O_2 = \underset{\text{Kinone.}}{C_6H_4O_2} + CO_2 + 4H_2O.$$

The same substance is obtained in a similar manner from one of the constituents of the coffee-berry (caffeic or caffeotannic acid). By dissolving kinone in water containing sulphurous acid gas, and evaporating the solution, colourless crystals of *hydrokinone* are obtained—



$$\underset{\text{Kinone.}}{C_6H_4O_2} + 2H_2O + SO_2 = \underset{\text{Hydrokinone.}}{C_6H_6O_2} + H_2O.SO_3.$$

When a solution of kinone is mixed with one of hydrokinone, beauti-

ful green crystals are deposited, which are known as *green hydrokinone* ($C_6H_4O_2.C_6H_6O_2$), and may also be obtained by the action of oxidising agents, such as ferric chloride, upon hydrokinone. When kinone is acted on with hydrochloric acid and chlorate of potash, it is converted into a yellow crystalline body, known as *perchlorokinole* or *chloranile* ($C_6Cl_4O_2$), which is also obtained in a similar way from aniline, salicine, and isatine. Potash dissolves it when heated, giving a purple solution.

423. *Theine* or *Caffeine—Tea—Coffee.*—A very remarkable instance of the application of chemistry to explain the use of widely different articles of diet by different nations, with a view to the production of certain analogous effects upon the system, is seen in the case of coffee, tea, Paraguay tea, and the *kola-nut* (of Central Africa), which are very dissimilar in their sensible properties, and afford little or no gratification to the palate, owing what attractions they possess chiefly to the presence, in each, of one and the same active principle or alkaloid, which has a special effect upon the animal economy. This alkaloid is known as caffeine or theine, and is associated in the three articles of diet mentioned above, with various substances, which give rise to their diversity in flavour.

The raw coffee-berry presents, on the average, the following composition:—

100 *parts of Raw Coffee contain*—

Woody fibre,	34·0
Water,	12·0
Fat,	12·0
Cane-sugar and gum,	15·5
Legumine, or some allied substance,	13·0
Caffeine,	1·5
Caffeic acid,	4·0
Mineral substances,	7·0

When the raw berry is treated with hot water, the infusion, which contains the sugar and gum, the legumine, caffeine, and *caffeic acid* ($C_{14}H_{16}O_7$), has none of the peculiar fragrance which distinguishes the ordinary beverage, and is due to an aromatic volatile oily substance termed *caffeone*, formed during the roasting to which the berry is subjected before use. This volatile oil, which is present in very minute quantity, is produced from one of the soluble constituents of the berry (probably from the caffeic acid), for if the infusion of raw coffee be evaporated to dryness, the residue, when heated, acquires the characteristic odour of roasted coffee.

The roasting is effected in ovens at a temperature rather below 400° F., when the berry swells greatly, and loses about $\frac{1}{4}$th of its weight, becoming brittle, and easily ground to powder. It also becomes very much darker in colour, from the conversion of the greater part of its sugar into caramel (p. 494), which imparts the dark-brown colour to the infusion of coffee. If the roasting be carried too far, a very disagreeable flavour is imparted to the coffee by the action of heat upon the legumine and other nitrogenised substances contained in the berry.

From 100 parts of the roasted coffee, boiling water extracts about 20 parts, consisting of caffeine, caffeic acid, caramel, legumine, a little suspended fatty matter, fragrant volatile oil (caffeone), and salts of potash (especially the phosphate). The undissolved portion of the coffee contains,

beside the woody fibre, a considerable quantity of nitrogenised (and nutritious) matter, and hence the custom, in some countries, of taking this residue together with the infusion.

In order to extract the caffeine from the infusion of coffee, it is mixed with solution of tribasic acetate of lead, to precipitate the caffeic acid and a part of the colouring matter. Through the filtered solution, sulphuretted hydrogen is passed to remove the lead as sulphide, and the liquid filtered from this is evaporated to a small bulk, when the caffeine crystallises out in white silky needles, which have a bitter taste, and the composition $C_8H_{10}N_4O_2.H_2O$. Its basic properties are very feeble.

The constituents of the leaves of the tea-plant (*Thea Sinensis*) exhibit a general similarity to those of the coffee-berry. In the fresh leaf we find, in addition to the woody fibre, a large quantity of a substance containing nitrogen, similar to legumine, an astringent acid similar to tannic acid, a small quantity of caffeine, and some mineral constituents.

The aroma of tea does not belong to the fresh leaf, but is produced, like that of coffee, during the process of drying by heat, which developes a small quantity of a peculiar volatile oil, having powerful stimulating properties. The freshly-dried leaf is comparatively so rich in this oil that it is not deemed advisable to use it until it has been kept for some time.

Green and black tea are the produce of the same plant, the difference being caused by the mode of preparation. For green tea the leaves are dried over a fire as soon as they are gathered, whilst those intended for black tea are allowed to remain exposed to the air in heaps for several hours, and are then rolled with the hands and partially dried over a fire, these processes being repeated three or four times to develope the desired flavour. The black colour appears to be due to the action of the air upon the tannin present in the leaf.

Boiling water extracts about 30 parts of soluble matter from 100 of black tea, and 36 from 100 of green tea. The principal constituents of the infusion of tea are tannin, aromatic oil, of which green tea contains about 0·8 and black tea 0·6 per cent., and caffeine, the proportion of which, in the dried leaf, varies from 2·2 to 4·1 per cent., being present in larger quantity in green tea.

The spent leaves contain the greater part of the legumine, and a considerable quantity of caffeine, which may be extracted by boiling them with water, and treating the decoction as above recommended in the case of coffee.

If tea be boiled with water, the solution precipitated with tribasic acetate of lead, the filtered liquid evaporated to dryness, and the residue cautiously heated, the caffeine sublimes in beautiful crystals.

Cocoa and *chocolate* are prepared from the cacao-nut, which is the seed of *Theobroma Cacao*, and is characterised by the presence of more than half of its weight (*minus* the husk) of a fatty substance known as *cacao-butter*, and consisting of oleine and stearine, which does not become rancid like the natural fats generally. The cacao-nut also contains a large quantity of starch, a nitrogenised substance resembling gluten, together with gum, sugar, and *theobromine*, a feeble base very similar to caffeine, but having the composition $C_7H_8N_4O_2$.

The seeds are allowed to ferment in heaps for a short time, which improves their flavour, dried in the sun and roasted like coffee, which developes the peculiar aroma of cocoa. The roasted beans having been

crushed and winnowed to separate the husks, are ground in warm mills, in which the fatty matter melts and unites with the ground beans to a paste, which is mixed with sugar and pressed into moulds. In the preparation of chocolate, vanilla and spices are also added.

From the composition of cocoa and chocolate it is seen that when consumed, as is usual, in the form of a paste, they would prove far more nutritious than mere infusions of tea and coffee.

Caffeine appears to be a methylated derivative from theobromine, for when it is boiled with potash, methylamine is evolved, and by acting with iodide of methyle (CH_3I) upon a silver-compound obtained from theobromine, $C_7(H_7Ag)N_4O_2$, the silver and methyle change places, yielding AgI and caffeine, $C_7H_7(CH_3)N_4O_2$ or methyle-theobromine.

424. The vegetable alkali *strychnine* ($C_{21}H_{22}N_2O_2$), only too well known for its activity as a poison, is contained in *crow-fig* or *Nux-vomica*, the seed of the poison-nut tree of the East Indies, and in several other plants of the same family. The strychnine appears to be combined, in the nux-vomica, with lactic acid, and is accompanied by a second alkaloid, *brucine* ($C_{23}H_{26}N_2O_4$). In order to extract it, the bruised seeds are boiled with water acidulated with hydrochloric acid, the solution is strained, and rendered alkaline by adding hydrate of lime, which displaces the strychnine and brucine from their combination with the acid, and separates them in the form of a precipitate. When this is boiled with alcohol, the excess of lime remains undissolved, whilst the strychnine and brucine are carried into solution; and since the former is less soluble in alcohol than the latter, it is deposited, before the brucine, on evaporating the liquid, in the form either of octahedral or prismatic crystals, which have an intensely bitter taste. This remarkable bitterness is one of the most prominent characters of strychnine; for although 7000 parts of water are required to dissolve one part of this alkaloid, the solution possesses an intolerably bitter flavour, even when further diluted with 100 times its weight of water. Chloroform and benzole both dissolve strychnine with great ease; and since these liquids refuse to mix with water, they are often employed to extract the poison from a large bulk of aqueous liquid by agitating it with a small quantity of one of them, which is then separated from the water and evaporated, in order to obtain the strychnine in the solid form. Very minute quantities may then be identified by moistening with strong sulphuric acid, and adding a minute quantity of chromate of potash, when the chromic acid acts upon the strychnine, giving rise to products of oxidation, which pervade the liquid in the form of beautiful purple streaks.

Curarine, $C_{10}H_{15}N$, is a crystalline alkaloid which has been extracted from the *woorari* or *curara* poison employed by the American Indians for poisoning arrows. It dissolves easily in water and alcohol, but not in ether. Strong sulphuric acid gives it a fine blue colour.

425. TOBACCO owes its active character chiefly to the presence of a vegetable alkali which is not found in any other plant than the *Nicotiana tabacum*, from the leaf of which the various forms of tobacco are manufactured. This alkali, *nicotine* ($C_{10}H_{14}N_2$), is distinguished from most others by the absence of oxygen, and by its liquid condition at the ordinary temperature.

In order to extract the nicotine from tobacco, the leaves are boiled with water, which dissolves the alkaloid, in combination with malic and citric acids. The liquid, having been strained, is evaporated to a syrup and mixed with alcohol, when it separates into two layers, of which the

upper contains the salts of nicotine dissolved in alcohol; the lower aqueous layer retaining the greater part of the extraneous vegetable matters. The alcoholic layer having been drawn off, is next shaken with potash, to combine with the acids, and with ether to dissolve the nicotine then set free. On decanting the ethereal solution of nicotine which rises to the surface, and evaporating the ether, the nicotine is left in the form of an oily liquid, which is colourless when perfectly pure, but soon acquires a dark brown colour when exposed to the air. It is very readily distinguished by its very pungent, irritating odour, recalling that of tobacco, and which is very perceptible at the common temperature, although the boiling point of nicotine is so high as 480° F. Water, alcohol, and ether dissolve nicotine with facility. The poisonous action of this alkaloid upon animals is very powerful, death almost immediately following its administration. The Virginian tobacco contains more nicotine than other varieties, the alkaloid amounting to nearly 7 per cent. of the weight of the leaf dried at 212° F., whilst the Maryland and Havannah varieties contain only 2 or 3 per cent. of nicotine. Tobacco is remarkable for the very large amount of ash which it leaves when burnt, amounting to about one-fifth of the weight of the dried leaf, and containing about one-third of carbonate of potash, resulting from the decomposition of the malate, citrate, and nitrate of potash during the combustion. The presence of this latter salt in large quantity (3 or 4 parts in 100 of the dried leaf) distinguishes tobacco from most other plants, and accounts for the peculiar smouldering combustion of the dried leaves.

Cigars are made directly from the tobacco leaves, which are only moistened with a weak solution of salt in order to impart the requisite suppleness; but *snuff*, after being thus moistened, is subjected, in large heaps, to a fermentation extending over eighteen or twenty months, which results in its becoming alkaline from the development of carbonate of ammonia (by the putrefaction of the vegetable albumen in the leaf) and of a minute quantity of free nicotine, which imparts the peculiar pungency to this form of tobacco. The aroma of the snuff appears to be due to the production of a peculiar volatile oil during the fermentation. The proportion of nicotine in snuff is only about two per cent., being one-third of that found in the unfermented tobacco; and a great part of this exists in the snuff in combination with acetic acid, which is also a result of the fermentation. It is also not improbable that a little acetic ether is produced, and perhaps some other acids and ethers of the acetic series (*e.g.*, butyric and valerianic), of which extremely minute quantities would give rise to great differences in the aroma of the snuff.

VEGETABLE COLOURING MATTERS.

426. Notwithstanding the great variety and beauty of the tints exhibited by plants, comparatively few yield colouring matters which are sufficiently permanent to be employed in the arts; the greater number of them fading rapidly as soon as the plant dies, since they are unable to resist the decomposing action of light, oxygen, and moisture, unless supported by the vital influence in the plant, some of them even fading during the life of the plant, as may be seen in some varieties of the rose, which are only fully coloured in those parts which have been partly obscured.

The green colouring matter of plants has been termed *chlorophyll*,* and is a resinous substance containing carbon, hydrogen, nitrogen, and oxygen, which has never yet been obtained in so pure a condition that its composition could be accurately determined, since it cannot be crystallised or distilled, aud is therefore not amenable to the usual methods by which organic substances are obtained in a pure state.

When green leaves are boiled with alcohol, the latter acquires a fine green colour, and, when evaporated, deposits the chlorophyll. When the alcoholic solution of chlorophyll is boiled with alcoholic solution of potash, and hydrochloric acid afterwards added, a yellow precipitate (*phylloxanthine*) is obtained, and a fine blue colouring matter (*phyllocyanine*) remains in solution. The blue matter contains nitrogen, and both are insoluble in water. The autumnal colour of leaves may possibly be due to the disappearance of the phyllocyanine. On immersing green leaves in chlorine they assume an autumnal tint.

The blue colouring matter contained in many flowers, such as the violet, has been named *cyanine*. Acids change its blue colour to red, and hence the blue colour is exhibited only by flowers the juice of which is neutral, whilst red flowers yield an acid juice. The colouring matter of grapes and of red wine appears to be identical with cyanine.

Two yellow colouring matters have been extracted from flowers, and have been named *xanthine* and *xanthéine*, the latter being soluble in water.

Saffron is a yellow colouring matter obtained from the flowers of the *Crocus sativus*, which are themselves of a blue colour, but have yellow anthers. When these are dried and pressed into cakes, they form the saffron of commerce, which is characterised by its very remarkable and somewhat agreeable odour. The yellow colouring matter is readily dissolved by water and alcohol, and has been found to be a glucoside, which yields, when treated with sulphuric acid, beside glucose, *crocine*, $C_{16}H_{18}O_6$, and an essential oil having the formula $C_{10}H_{14}O$.

Safflower consists of the petals of the *Carthamus tinctorius*, a plant cultivated in Egypt. It furnishes a red colouring matter called *carthamine* ($C_{14}H_{16}O_7$), which is used in dyeing, although it fades easily when exposed to light. It exhibits the characters of an acid, being dissolved by alkalies and reprecipitated by acids, a circumstance which is taken advantage of when extracting it from the safflower.

The orange-yellow colouring matter known as *annatto* is extracted from the seeds of the *Bixa Orellana*, a native of the West Indies. The colouring principle has been called *bixine*, and is dissolved by alkalies, but precipitated again by acids. Annatto is used for colouring butter and cheese.

A valuable yellow colour is obtained from the *weld*, or *Reseda luteola*,

* Χλωρός, *green*; φύλλον, *a leaf*.

by boiling the dried leaves with water. This colouring matter is termed *luteoline* ($C_{20}H_{14}O_6$), and may be sublimed in yellow needles.

The woods of various trees, when boiled with water, furnish colouring matters of considerable importance; thus, the wood of *Morus tinctoria*, or *fustic*, a West Indian tree, yields a crystalline yellow colour called *moritannic acid* ($C_{18}H_{16}O_{10}$).

Logwood is the wood of the *Hæmatoxylon Campechianum*, which grows at Campeachy, in the Bay of Honduras. Its most important constituent is a yellow colouring matter called *hæmatoxyline*, which may be obtained in needle-like crystals having the composition ($C_{16}H_{14}O_6$,Aq.) It becomes intensely red in contact with alkalies and oxygen, from the formation of hæmatein ($C_{16}H_{12}O_6$). Chromate of potash gives an intense black colour with infusion of logwood, which has been used as an ink, but is not permanent.

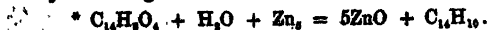
Brazil wood, which is employed in the preparation of red ink, contains a colouring matter somewhat resembling that of logwood.

The well-known Turkey red colour is obtained from *madder*, the root of the *Rubia tinctorum*, imported from the south of France and the Levant. This root does not contain any red colouring matter during the life of the plant, but a yellow substance (*rubian*, $C_{28}H_{34}O_{15}$), from the decomposition of which the madder red is obtained. There are several methods in use for obtaining the red colour from madder. If the root be steeped in water for some time, so that some of the nitrogenised constituents begin to undergo decomposition, a peculiar fermentation is excited in the rubian, resulting in its decomposition into several new bodies, the chief of which are a red crystalline colouring matter, *alizarine* ($C_{14}H_8O_4$), and an uncrystallisable sugar. The alizarine may be dissolved out either by water or alcohol, and may be obtained in beautiful plates having a golden lustre.

If the madder root be boiled with water, the rubian is dissolved, and when this solution is boiled with dilute sulphuric acid, the rubian undergoes a decomposition similar to that mentioned above, and the alizarine, being insoluble in the dilute acid, is precipitated.

Madder which has been treated with hot sulphuric acid, so as to decompose the rubian, is used in print-works under the name of *garancine*, and yields a red solution containing alizarine when boiled with water.

Artificial alizarine.—The discovery of a process for the artificial production of the colouring matter of madder from anthracene, one of the constituents of coal-tar, is one of the most important services which chemistry has, of late years, rendered to the useful arts, and affords an excellent illustration of the practical importance of the minute study of the constitution of organic substances. When alizarine, $C_{14}H_8O_4$, was heated with powdered zinc, it was found to be converted into *anthracene*, $C_{14}H_{10}$, a substance obtained among the last products of the distillation of coal-tar, for which no useful application had hitherto been discovered.* It somewhat resembles naphthaline in properties, but may be distinguished from it by its sparing solubility in alcohol. When treated with nitric acid, or with sulphuric acid and binoxide of manganese, it yields a crystalline compound known as *oxanthracene*, $C_{14}H_8O_2$, which bears the same relation to anthracene as quinone (p. 586) ($C_6H_4O_2$) bears to benzole (C_6H_6), and has therefore been called *anthraquinone*. When acted upon by bromine, this is converted into *dibromanthraquinone*, $C_{14}H_6Br_2O_2$. By heating this to about 350° F. with caustic potash,


* $C_{14}H_8O_4 + H_2O + Zn_5 = 5ZnO + C_{14}H_{10}$.

$C_{14}H_6Br_2O_2 + 4KHO = C_{14}H_6K_2O_4$ (*potassic alizarate*) + 2KBr + $2H_2O$. Alizarine is precipitated by decomposing the potassic alizarate with hydrochloric acid, $C_{14}H_6K_2O_4 + 2HCl = C_{14}H_8O_4$ (*alizarine*) + 2KCl. A cheaper process for the artificial formation of alizarine consists in heating the anthraquinone with oil of vitriol, so as to convert it into disulphanthroquinonic acid, which is afterwards converted into potassic alizarate by being heated with caustic potash; $C_{14}H_8O_2$, (*anthraquinone*) + $2(H_2.SO_3.O_2)$ (*oil of vitriol*) = $C_{14}H_8.(SO_2)_2.O_4$ (*disulphoanthraquinonic acid*) + $2H_2O$. When this acid is heated to about 350° F. with caustic potash, $C_{14}H_8(SO_2)_2.O_4 + 6KHO = C_{14}H_6K_2O_4$ (*potassic alizarate*) + $2(K_2O.SO_2)$ + $4H_2O$.

The scientific interest of this production of alizarine from anthracene is enhanced by the circumstance that anthracene has itself been produced by synthesis; for carbon and hydrogen combine, at a high temperature, to produce acetylene (C_2H_2), three molecules of which coalesce at a high temperature to form benzole (C_6H_6), and by acting upon two molecules of benzole with one molecule of ethylene, anthracene has been produced, $2C_6H_6 + C_2H_4 = C_{14}H_{10} + H_6$.

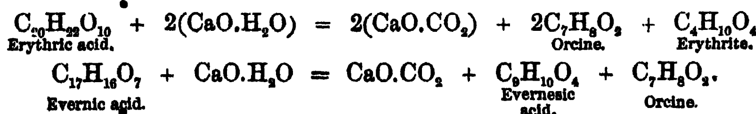
Turmeric is the root of an East Indian plant, the *Curcuma longa*; its colouring matter, called *curcumine*, is nearly insoluble in water, but dissolves in alcohol. Its yellow colour is changed to brown by alkalies, which leads to its use in the laboratory as a test of alkalinity.

427. *Litmus, archil,* and *cudbear* are brilliant, though not very permanent purple and violet colours, prepared from various lichens, such as *Roccella tinctoria* (litmus), and *Lecanora tartarea* (cudbear*).

Archil and cudbear owe their colour chiefly to the presence of *orcéine* ($C_7H_7NO_3$), which does not exist ready formed in any of the lichens, but is developed during the preparation which they undergo.

If either of the above lichens be digested for some hours with lime and water, and the filtered solution be neutralised with hydrochloric acid, a white gelatinous precipitate is obtained, which dissolves in hot alcohol, and is deposited in crystals on cooling. This substance may consist, according to the particular lichen employed, of one or more acids, the chief of which have been named *erythric* ($C_{20}H_{22}O_{10}$), *evernic* ($C_{17}H_{16}O_7$), and *lecanoric* ($C_8H_8O_4$) acids. These acids are remarkable for the facility with which they furnish compound ethers when boiled with alcohol.

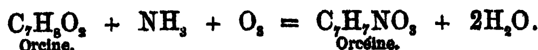
When either of these acids is boiled with an excess of lime or baryta, it is decomposed, and if the excess of base be removed by carbonic acid, the filtered liquid evaporated to a syrup, and extracted with boiling alcohol, the latter deposits prismatic crystals of *orcine* ($C_7H_8O_2$.Aq.) The formation of this body will be understood from the following equations—



$$\underset{\text{Erythric acid.}}{C_{20}H_{22}O_{10}} + 2(CaO.H_2O) = 2(CaO.CO_2) + \underset{\text{Orcine.}}{2C_7H_8O_2} + \underset{\text{Erythrite.}}{C_4H_{10}O_4}$$

$$\underset{\text{Evernic acid.}}{C_{17}H_{16}O_7} + CaO.H_2O = CaO.CO_2 + \underset{\text{Evernesic acid.}}{C_9H_{10}O_4} + \underset{\text{Orcine.}}{C_7H_8O_2}.$$

Pure orcine is a colourless substance, but when exposed to the joint action of ammonia and air, it is converted into a beautiful red colouring matter, *orcéine*—



$$\underset{\text{Orcine.}}{C_7H_8O_2} + NH_3 + O_2 = \underset{\text{Orcéine.}}{C_7H_7NO_3} + 2H_2O.$$

* Said to have been named after Cuthbert, a manufacturer of the dye.

Orcéine does not crystallise, and dissolves to a slight extent only in water, but readily in alcohol and in alkaline liquids, yielding, in the latter case, a beautiful purple solution, which becomes red when mixed with acids, and deposits red flakes of orcéine.

The chemistry of the processes by which archil and cudbear are prepared will now be easily understood. The powdered lichen is mixed with urine (to furnish ammonia) and lime, and exposed to the air for some weeks, when the lime decomposes the erythric and other acids, with formation of orcine, which then passes into orcéine under the influence of the ammonia and atmospheric oxygen.

The preparation of litmus from the *Roccella tinctoria* is similar to that just described, but a mixture of carbonate of ammonia and carbonate of potash is employed instead of the urine and lime. The chemical change which takes place, although similar in principle, is not precisely identical with the foregoing, for the principal colouring matter developed appears to be a red substance called *azolitmine* ($C_9H_{10}NO_5$), which differs from orcéine by its insolubility in alcohol. It dissolves in alkaline solutions with a beautiful blue colour, which is immediately reddened by acids, a property frequently turned to account by the chemist for detecting the acid reaction. Litmus occurs in commerce in small cakes, which are made up with chalk.

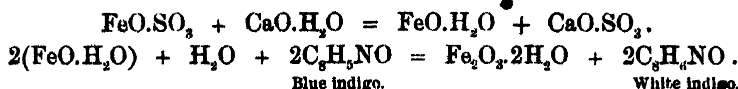
Erythrite ($C_4H_{10}O_4$) is a crystalline substance extracted from various lichens and fungi, which forms combinations with the fatty acids similar to those formed by glycerine. It is sometimes represented as a tetratomic alcohol (p. 554), $(C_4H_6)^{iv}H_4.O_4$.

428. *Indigo blue* (C_8H_5NO) is prepared from various species of *Indigofera*, grown in China, India, and America. The plants are covered with cold water and allowed to ferment; as soon as a blue scum appears upon the surface, a little lime is added and the mixture stirred briskly for some time, when the indigo is deposited in a pulverulent form; it is collected on calico strainers, pressed and cut up into cakes.

The theory of the process is not yet clearly explained; it is certain that the indigo blue does not pre-exist in the plant, but is a product of the fermentation. Recent observations have shown that the indigo plants probably contain a substance called *indican* ($C_{26}H_{33}NO_{18}$), which stands in a similar relation to indigo blue to that in which rubian stands to alizarine (in the case of madder); it is soluble in water, and when heated with an acid, splits up into indigo blue, *indigo red*, and a peculiar uncrystallisable sugar. The indigo red may be extracted from commercial indigo by boiling with alcohol, in which the indigo blue is insoluble. Since indigo blue is insoluble in all ordinary solvents, it is necessary, in order to use it for dyeing, to reduce it to the condition of *white indigo*, which is soluble in alkalies.

If 2 parts of protosulphate of iron (copperas) be dissolved in 200 parts of water, and well shaken in a stoppered bottle with 1 part of powdered indigo and 3 of slaked lime, the indigo will disappear, and on allowing the precipitate to subside, a yellow fluid will be obtained, which becomes blue at the surface as soon as it is exposed to air. If this solution be mixed with hydrochloric acid, out of contact with air, a flocculent precipitate of *white indigo* is obtained. The composition of this substance is C_8H_6NO; and it is formed from blue indigo (C_8H_5NO) by the addition of an atom of hydrogen derived from water, the oxygen of which has com-

bined with the protoxide of iron ; one portion of the lime combines with the sulphuric acid of the sulphate of iron, whilst another serves to dissolve the white indigo, which is soluble in alkaline liquids—



$$FeO.SO_3 + CaO.H_2O = FeO.H_2O + CaO.SO_3.$$
$$2(FeO.H_2O) + H_2O + \underset{\text{Blue indigo.}}{2C_8H_5NO} = Fe_2O_3.2H_2O + \underset{\text{White indigo.}}{2C_8H_6NO}.$$

The solution of white indigo prepared by this process is employed for dyeing linen and cotton, which are immersed in the vat, and then exposed to the air, the oxygen of which removes an atom of hydrogen from the white indigo, and the blue indigo thus formed is precipitated upon the fibre.

Other reducing agents are sometimes substituted for the protosulphate of iron. Even decaying vegetable matter effects the conversion of blue into white indigo in an alkaline liquid. Thus, for some purposes, the vat is prepared by fermenting a mixture of indigo, madder, carbonate of potash, and lime, when the hydrogen extricated in the fermentation of the vegetable matter converts the blue into white indigo, which is then dissolved by the potash liberated from the carbonate by the lime.

When cloth is dyed with indigo (Saxony blue) the colour is dissolved by means of sulphuric acid. Fuming sulphuric acid dissolves indigo blue very readily, but oil of vitriol does not act quite so well. The solution thus obtained is commonly called *sulphindigotic acid*, but it really contains two acids, the *sulphindylic* ($HC_8H_4NO.SO_3$) and *hyposulphindigotic*. The blue solution becomes colourless when shaken with powdered zinc, and resumes its blue colour when shaken with air.

On heating indigo, it evolves purple vapours, which condense in prismatic crystals of a coppery lustre, consisting of pure *indigotine* or indigo blue (C_8H_5NO), which may be obtained in larger quantity by digesting indigo with grape-sugar, caustic soda, and weak alcohol, when a solution of white indigo is obtained which deposits the crystallised indigotine on exposure to air.

429. *Animal colouring matters.*—From the animal kingdom only two colouring matters of any great importance are derived, viz., cochineal and lac, both which are obtained from insects of the *coccus* tribe. The colouring matter of cochineal is known as *carmine,* and may be extracted from the insects by water or alcohol. It has acid properties, and has been named *carminic acid* ($C_{14}H_{14}O_8$). *Carmine-lake* is a combination of this acid with alumina, precipitated when a solution of alum and an alkaline carbonate are added to one of cochineal.

DYEING AND CALICO PRINTING.

430. The object of the dyer being to fix certain colouring matters permanently in the fabric, his processes would be expected to vary with the nature of the latter and of the colour to be applied to it. In order that uniformity of colour and its perfect penetration into the fibre may be attained, it is evident that the colouring matter must always be employed in a state of solution ; and it must be rendered *fast,* or not removable by washing, by assuming an insoluble condition in the fibre. The simplest form of dyeing is that in which the fibre itself forms an in-

soluble compound with the colouring matter. Thus, if a skein of silk be immersed in a solution of indigo in sulphuric acid, it removes the whole of the colouring matter from the liquid, and may then be washed with water without losing colour; but if the same experiment be tried with cotton, the indigo will not be withdrawn from the solution, and when the cotton has been well squeezed and rinsed with water, it will become white again. It may be stated generally, that the animal fabrics (silk and wool) will absorb and retain colouring matters with much greater facility than vegetable fabrics (cotton and linen). In the absence of so powerful an attraction between the fibre and the colouring matter, it is usual to impregnate the fabric with a *mordant* or substance having an attraction for the colour, and capable of forming an insoluble combination with it, so as to retain it permanently attached to the fabric. Thus, if a piece of cotton be boiled in a solution of acetate of alumina, the alumina will be precipitated in the fibre; and if the cotton be then soaked in solution of cochineal or of logwood, the red colouring matter will form an insoluble compound (or *lake*) with the alumina, and the cotton will be dyed of a fast red colour.

Another method of fixing the colour in the fabric consists in impregnating the latter with two or more liquids in succession, by the admixture of which the colour may be produced in an insoluble state. If a piece of any stuff be soaked in solution of perchloride of iron, and afterwards in ferrocyanide of potassium, the Prussian blue which is precipitated in the fibre will impart a fast blue tint.

An indispensable preliminary step to the dyeing of any fabric is the removal of all natural grease or colouring matter, which is effected by processes varying with the nature of the fibre, and is preceded, in the cases of cotton and woollen materials which are to receive a pattern, by certain operations of shaving and singeing, for removing the short hairs from the surface.

From linen and cotton, the extraneous matters (such as grease and resin) are generally removed by weak solutions of carbonate of potash or of soda, and the fabrics are afterwards bleached by treatment with chloride of lime (p. 151). But since the fibres of silk and wool are much more easily injured by alkalies and by chlorine, greater care is requisite in cleansing them. Silk is boiled with a solution of white soap to remove the *gum*, as it is technically termed; but the natural grease is extracted from wool by soaking at a moderate temperature in a weak bath either of soap or of ammoniacal (putrefied) urine. Both silk and wool are bleached by sulphurous acid (p. 200).

Among the red dyes the most important are madder, Brazil wood, cochineal, lac, and the colours derived from aniline.

In dyeing red with madder or Brazil wood, the linen, cotton, or wool is first mordanted by boiling in a solution containing alum and bitartrate of potash, when it combines with a part of the alumina, and on plunging the stuff into a hot infusion of madder, the colouring matter forms an insoluble combination with that earth.

To dye Turkey-red, the stuff is also mordanted with alum, but has previously to undergo several processes of treatment with oil and with galls, the necessity of which is satisfactorily established in practice, though it is not easy to explain their action. The colour is finally brightened by boiling the stuff with chloride of tin.

Woollen cloth is dyed scarlet with lac or cochineal, having been first

mordanted by boiling in a mixture of perchloride of tin and bitartrate of potash.

The aniline colours (see p. 451) are employed for dyeing silk and wool, either without any mordant or with the help of albumen.

Blues are generally dyed with indigo (p. 595), or with Prussian blue; in the latter case the stuff is steeped successively in solutions of a salt of peroxide of iron and of ferrocyanide of potassium. Aniline blue is also much employed for silk and woollen fabrics.

The principal yellow dyes are weld, quercitron, fustic, annatto, chrysaniline, and chromate of lead. For the four first colouring matters aluminous mordants are generally applied. Chromate of lead is produced in the fibre of the stuff, which is soaked for that purpose, first in a solution of acetate or nitrate of lead, and then in chromate of potash.

Carbazotic acid (p. 456) is also sometimes employed as a yellow dye.

In dyeing blacks and browns, the stuffs are steeped first in a bath containing some form of tannin (p. 581), such as infusion of galls, sumach, or catechu, and afterwards in a solution of a salt of iron, different shades being produced by the addition of indigo, of sulphate of copper, &c.

431. The art of calico-printing differs from that of dyeing, in that the colour is required to be applied only to certain parts of the fabric, so as to produce a pattern or design either of one or of several colours.

A common method of printing a coloured pattern upon a white ground consists in impressing the pattern by passing the stuff under a roller, to which an appropriate mordant thickened with British gum (p. 481) is applied. The stuff is then *dunged*, *i.e.*, drawn through a mixture of cow-dung and water, which appears to act by removing the excess of the mordant, and afterwards immersed in the hot dye-bath, when the colour becomes permanently fixed to the mordanted device, but may be removed from the rest of the stuff by washing.

If the pattern be printed with a solution of acetate of iron, and the stuff immersed in a madder-bath, a lilac or black pattern will be obtained according to the strength of the mordant employed. By using acetate of alumina as a mordant, the madder-bath would give a red pattern.

A process which is the reverse of this is sometimes employed, the pattern being impressed with a *resist*, that is, a substance which will prevent the stuff from taking the colour in those parts which have been impregnated with it. For example, if a pattern be printed with thickened tartaric or citric acid, and the stuff be then passed through an aluminous mordant, the pattern will refuse to take up the alumina, and subsequently, the colour from the dye-bath. Or a pattern may be printed with nitrate of copper, and the stuff passed through a bath of reduced indigo (p. 594), when the nitrate of copper will oxidise the indigo, and by converting it into the blue insoluble form, will prevent it from sinking into the fibre of those parts to which the nitrate has been applied, whilst elsewhere, the fibre, having become impregnated with the white indigo, acquires a fast blue tint when exposed to the air.

Sometimes the stuff is uniformly dyed, and the colour discharged in order to form the pattern. A white pattern is produced upon a red (madder) or blue (indigo) ground by printing with a thickened acid discharge, and passing the stuff through a weak bath of chloride of lime, which removes the colour from those parts only which were impregnated with the acid (p. 151). By adding nitrate of lead to the acid discharge,

and finally passing the stuff through solution of chromate of potash, a yellow pattern (chromate of lead) may be obtained upon the madder red ground.

By applying nitric acid as a discharge, a yellow pattern may be obtained upon an indigo ground (p. 131).

Very brilliant designs are produced by mordanting the stuff in a solution of stannate of potash or soda (p. 383), and immersing it in dilute sulphuric acid, which precipitates the stannic acid in the fibre. When the thickened colouring matters are printed on in patterns, and exposed to the action of steam, an insoluble compound is formed between the colour and the stannic acid, which usually exhibits a very fine and permanent colour.

It is evident that by combining the principles of which an outline has just been given, the most varied parti-coloured patterns may be printed.

ANIMAL CHEMISTRY.

432. Our acquaintance with the chemistry of the substances composing the bodies of animals is still very limited, although the attention of many accomplished investigators has been directed to this branch of the science. The reasons for this are to be found, firstly, in the susceptibility to change exhibited by animal substances when removed from the influence of life; and secondly, in the absence, in such substances, of certain physical properties by which we might be enabled to separate them from other bodies with which they are associated, and to verify their purity when obtained in a separate state. Two of the most important of these properties are volatility and the tendency to crystallise. When a substance can suffer distillation without change, it will be remembered that its boiling point affords a criterion of its purity; or if it be capable of crystallising, this may be taken advantage of in separating it from other substances which crystallise more or less easily than itself, and its purity may be ascertained from the absence of crystals of any other form than that belonging to the substance. But the greater number of the components of animal frames can neither be crystallised nor distilled, so that many of the analyses which have been made of such substances differ widely from each other, because the analyst could never be sure of the perfect purity of his material; and even when concordant results have been obtained as to the percentage composition of the substance, the atomic formula deduced from it has been of so singular and exceptional a character as to cast very strong suspicion upon the purity of the substance.

Accordingly, the chemical formulæ of a great many animal substances are perfectly unintelligible, conveying not the least information as to the position in which the compound stands with respect to other substances, or the changes which it might undergo under given circumstances.

It has been shown in the previous chapters of this work that we are gradually learning to class all compound bodies under a few typical forms, so that the chemical properties of any substance may in many cases be predicted from its composition as indicating the type to which it belongs. Take, for example, the class of alcohols ($C_nH_{2n+2}O$), or of volatile acids ($C_nH_{2n}O_2$), or of ammonias (XY_3), and it will be seen that even those formulæ which are apparently the most complex, are perfectly intelligible

when referred to their proper type (p. 534). But the extraordinary formulæ, for example, deduced from the ultimate analysis of



Albumen, $C_{108}H_{169}N_{27}O_{34}S$ and



Caseine, $C_{144}H_{228}N_{36}O_{45}S$

cannot be referred to any known type, and refuse to be classed with other substances, even if a type were invented expressly for them.

Animal chemistry is for the above reasons in a very backward condition, as compared with vegetable and mineral chemistry, though an observation of the progress of research affords us the consolation, that a steady advance is being made towards a generalisation of the facts which have been discovered, especially by analogical reasoning from those two other departments of the science.

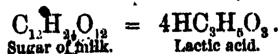
Milk.—The chemistry of milk is well adapted to introduce the study of animal chemistry, because that liquid contains representatives of all the substances which make up the animal frame ; and it is on this account that it occupies so high a position among articles of food.

Although, to the unaided eye, milk appears to be a perfectly homogeneous fluid, the microscope reveals the presence of innumerable globules floating in a transparent liquid, which is thus rendered opaque. If milk be very violently agitated for several hours, masses of an oily fat (butter, p. 572) are separated from it, and leave the liquid transparent. This fat was originally distributed throughout the milk in minute globules enclosed in very thin membranes, which were torn by the violent agitation, and the fatty globules then cohered into larger masses.

For the preparation of butter, it is usual to allow the milk to stand for some hours, when a layer of *cream* collects upon the surface, the proportion of which is very variable, but is generally about $\frac{1}{10}$th of the volume of the milk. The *skimmed milk* retains about half of the fatty matter. This cream contains about 5 per cent. (by weight) of fat, 3 per cent. of caseine, and water. When the cream is *churned*, the enclosing membranes of the fat globules are broken, and the fat unites into a semi-solid mass of butter, from which the butter-milk containing the caseine may be separated. If this be not done effectually, the caseine which is left in the butter, being a nitrogenised substance, will soon begin to decompose, and will induce a decomposition in the butter (p. 572), resulting in the elimination of certain volatile acids, which impart to it a rancid and offensive taste and odour. To prevent this, salt is generally added to butter which has been less carefully prepared, in order to preserve the caseine from decomposition. *Butter-milk* contains about one-fourth of the fatty matter of the milk.

Pure butter is essentially a mixture of margarine and oleine with smaller quantities of other fats, such as butyrine, caprine, and caproine (p. 572).

Fresh milk is slightly alkaline to test-papers, but after a short time it acquires an acid reaction ; and if it be then heated, it coagulates from the separation of the caseine. This spontaneous acidification of milk is caused by the fermentation of the *sugar of milk*, under the influence of the caseine, which results in the production of *lactic acid*, according to the equation—



$$\underset{\text{Sugar of milk.}}{C_{12}H_{24}O_{12}} = \underset{\text{Lactic acid.}}{4HC_3H_5O_3}.$$

The caseine, being insoluble in the acid fluid, separates in the form of curd. This development of lactic acid is spoken of as the *lactic fermen-*

tation, and may be excited not only in milk sugar, but in other substances analogous to it. This is taken advantage of in the preparation of lactic acid, for which purpose 8 parts of cane-sugar are dissolved in 50 parts of water, and 1 part of poor cheese with 3 parts of chalk are added to the mixture, which is then allowed to remain for some weeks at about 80° F. The lactic acid formed from the cane-sugar ($C_{12}H_{22}O_{11}$), under the influence of the changing caseine in the cheese, combines with the lime of the chalk, disengaging the carbonic acid, and forming crystals of lactate of lime ($Ca2C_3H_5O_3$). This is dissolved in boiling water, recrystallised in order to purify it, and digested with one-third of its weight of sulphuric acid, which converts the lime into sulphate, liberating the lactic acid; by adding alcohol, the whole of the sulphate of lime is precipitated, and the lactic acid is dissolved by the alcohol, which leaves it on evaporation as a colourless, syrupy, very acid liquid, which may be distilled, though with some loss from decomposition, if heated out of contact with air.

By heating lactic acid to about 270° F. for a considerable length of time, a molecule of water is expelled, and the lactic anhydride ($C_6H_{10}O_5$) is left as a brownish glassy substance, which is reconverted into the acid by boiling with water. At a temperature of 500° F. lactic acid undergoes a destructive distillation, the most interesting product of which is a transparent crystalline substance called lactide ($C_3H_4O_2$) differing from lactic acid by the elements of water, which it resumes when dissolved in that liquid, being converted into lactic acid ($C_3H_6O_3$). When lactic acid is heated with hydriodic acid in a sealed tube, it is converted into propionic acid—



$$HC_3H_5O_3 \text{ (Lactic acid)} + 2HI = HC_3H_5O_2 \text{ (Propionic acid)} + H_2O + I_2.$$

Lactic acid is an important constituent of the animal body, being found in the juice of muscular flesh, in the gastric juice, &c.

If milk be maintained at a temperature of about 90° F., the fermentation induced by the caseine results in the production of alcohol and carbonic acid, for although milk-sugar is not fermented like ordinary sugar by contact with yeast, it appears, under the influence of the changing caseine at a favourable temperature, to be converted first into grape-sugar (p. 485), and afterwards into alcohol and carbonic acid. The Tartars prepare an intoxicating liquid, which they call *koumiss*, by the fermentation of milk.

When an acid is added to milk, the caseine is separated in the form of curd, in consequence of the neutralisation of the soda which retains it dissolved in fresh milk, and this curd carries with it, mechanically, the fat globules of the milk, leaving a clear yellow *whey*.

In the preparation of cheese, the milk is coagulated by means of *rennet*, which is prepared from the lining membrane of a calf's stomach. This is left in contact with the warm milk for some hours, until the coagulation is completed. This action of rennet upon milk has not yet received any satisfactory explanation. The curd is collected and pressed into cheeses, which are allowed to ripen in a cool place, where they are occasionally sprinkled with salt. The peculiar flavour which the cheese thus acquires is due to the decomposition of the fatty matter under the influence of the caseine, giving rise to the production of certain volatile acids, such as butyric, valerianic, and caproic, which have very powerful and characteristic odours. If this ripening be allowed to proceed very far, ammonia is developed by the putrefaction of the caseine, and in some cases the ethers of the above-

mentioned acids are produced, at the expense probably of a little sugar of milk left in the cheese, conferring the peculiar aroma perceptible in some varieties of it.

The different kinds of cheese are dependent upon the kind of milk used in their preparation, the richer cheeses being, of course, obtained from milk containing a large proportion of cream; such cheese fuses at a moderate heat, and makes good toasted cheese, whilst that which contains little butter never fuses completely, but dries and shrivels like leather.

Double Gloucester and Stilton are made from a mixture of new milk and cream. Chedder cheese is made from new milk alone. Cheshire and American cheeses, from milk robbed of about one-eighth of its cream. Dutch cheese and the *Skim Dick* of the midland counties, from skimmed milk.

Caseine.—The pure curd of milk is known as caseine and consists essentially of carbon, hydrogen, nitrogen, oxygen, and a small proportion (one per cent.) of sulphur. The simplest expression of the result of the analysis of caseine, in formula, would be $C_{144}H_{228}N_{36}O_{45}S$, but the anomalous complexity of this formula conveys a suspicion that the composition of pure caseine has yet to be fixed. By whatever process it has been purified, hitherto it has always been found to retain saline matters. The complexity of its composition accounts for its liability to undergo putrefactive decomposition.

Coagulated caseine is characterised by the facility with which it is dissolved by alkaline solutions, such as carbonate of soda, yielding a liquid upon the surface of which, when boiled, an insoluble pellicle forms, exactly similar to that which forms upon the surface of boiled milk. Coagulated caseine may also be dissolved by acetic or oxalic acid, but the addition of sulphuric or hydrochloric acid reprecipitates it, these acids apparently forming insoluble compounds with caseine.

If skimmed milk be carefully evaporated to dryness, and the fat extracted from the residue by ether, the caseine is left in the soluble form mixed with milk-sugar, and is capable of dissolving in water or in weak alcohol.

Caseine appears to possess the properties of a weak acid, since it combines both with the alkalies and alkaline earths, and is even said to be capable of partially neutralising the former. A mixture of cheese and slaked lime is sometimes used as a cement for earthenware, the caseine combining with the lime to form a hard insoluble mass. The curd of milk, washed and dried, is used by calico-printers, under the name of *lactarine*, for fixing colours. If it be dissolved in weak ammonia, mixed with one of the aniline dyes, printed on calico, and steamed, the ammonia is expelled, and the colour is left behind as an insoluble compound with the caseine.

Caseine, or a substance so closely resembling it as to be easily confounded with it, is found in peas, beans, and most leguminous seeds. If dried peas be crushed and digested for some time in tepid water, a turbid liquid is obtained, holding starch in suspension. If this be allowed to settle, the clear liquid is an impure aqueous solution of *legumine*, or vegetable caseine, which constitutes about one-fourth of the weight of the peas.

This solution is not coagulated by heat, but becomes covered with a pellicle similar to that which forms upon the surface of boiled milk. It is coagulated by acetic acid and by rennet, just as is the case with the caseine of milk.

Sugar of milk.—When whey is evaporated to a small bulk and allowed

to cool, it deposits hard white prismatic crystals of sugar of milk, or lactine ($C_{12}H_{24}O_{12}$), which is much less soluble, and therefore less sweet than cane-sugar.

Like this latter it may be converted into grape-sugar ($C_6H_{14}O_7$) by taking up the elements of two molecules of water when boiled with dilute acids. Milk-sugar resembles the other sugars in its capability of combining with some bases, such as the alkalies, alkaline earths, and oxide of lead; with the latter it forms two insoluble compounds.

At about 280° F. the crystals of milk-sugar lose a molecule of water and become $C_{12}H_{22}O_{11}$. At 400° F. the sugar fuses, and two molecules lose five molecules of water.

It will be seen that the characteristic constituents of milk are the caseine and milk-sugar, but the proportions in which these are present vary widely, not only with the animal from which the milk is obtained, but with the food and condition of the animal. A general notion of their relative quantities, however, may be gathered from the following table, exhibiting the results of the analyses made by Boussingault:—

	Cow.	Ass	Goat.	Woman.
Water, . . .	87·4	90·5	82·0	88·4
Butter, . . .	4·0	1·4	4·5	2·5
Milk-sugar, Soluble salts,	5·0	6·4	4·5	4·8
Caseine, Insoluble salts,	3·6	1·7	9·0	3·8

The soluble salts present in milk include the phosphates of potash and soda, and the chlorides of potassium and sodium, whilst the insoluble salts are the phosphates of lime, magnesia, and oxide of iron. All these salts are in great request for the nourishment of the animal frame.

The milk supplied to consumers living in towns is subject to considerable adulteration; but in most cases this is effected by simply removing the cream and diluting the skimmed milk with water, a fraud which is not easily detected, as might be supposed, by determining the specific gravity of the milk, for since milk is heavier than water (1·032 sp. gr.), and the fatty matter composing cream is lighter than water, a certain quantity of cream might be removed, and water added, without altering the specific gravity of the milk.

The most satisfactory method of ascertaining the quality of the milk appears to consist in setting it aside for twenty-four hours in a tall narrow tube (*lactometer*), divided into 100 equal parts, and measuring the proportion of cream which separates, this averaging, in pure milk, from eleven to thirteen divisions. By shaking milk with a little potash (to dissolve the membrane which envelopes the fat globules) and ether, the butter may be dissolved in the ether which rises to the surface, and if this be poured off and allowed to evaporate, the weight of the butter may be ascertained. 1000 grains of milk should give, at least, 27 or 28 grains of butter. Since, however, the milk of the same cow gives very different quantities of cream at different times, it is difficult to state confidently that adulteration has been practised. It is said that certain yellow colouring matters, such as annatto and turmeric, as well as gum, starch, &c., are occasionally employed to confer an appearance of richness upon impoverished milk.

433. Blood.—The blood from which the various organs of the body directly receive their nourishment is the most important, as well as the most complex of the animal fluids. Its chemical examination is attended with much difficulty, on account of the rapidity with which it changes after removal from the body of the animal.

On examining freshly drawn blood under the microscope, it is observed to present some resemblance to milk in its physical constitution, consisting of opaque flattened globules floating in a transparent liquid; the globules, in the case of blood, having a well-marked red colour.

In a few minutes after the blood has been drawn, it begins to assume a gelatinous appearance, and the semi-solid mass thus formed separates into a red solid portion or *clot*, which continues to shrink for ten or twelve hours, and a clear yellow liquid or *serum*. It might be supposed that this coagulation is due to the cooling of the blood, but it is found by experiment to take place even more rapidly when the temperature of the blood is raised one or two degrees after it has been drawn; and on the other hand, if it be artificially cooled, its coagulation is retarded. Indeed, the reason for this remarkable behaviour of the blood is not yet understood.

If the coagulum or clot of blood be cut into slices, tied in a cloth, and well washed in a stream of water, the latter runs off with a bright red colour, and a tough yellow filamentous substance is left upon the cloth; this substance is called *fibrine*, and its presence is the proximate cause of the coagulation of the blood, for if the fresh blood be well whipped with a bundle of twigs or glass rods, the fibrine will adhere to them in yellow strings, and the *defibrinated* blood will no longer coagulate on standing. If this blood, from which the fibrine has been extracted, be mixed with a large quantity of a saline solution (for example, 8 times its bulk of a saturated solution of sulphate of soda), and allowed to stand, the red globules subside to the bottom of the vessel.

These globules are minute bags of red fluid, enclosed in a very thin membrane or *cell-wall*, and if water were mixed with the defibrinated blood, since its specific gravity is lower than that of the fluid in the globules, it would pass through the membrane (by *endosmose*), and so swell the latter as to break it and disperse the contents through the liquid.

The red fluid contained in these blood globules consists of an aqueous solution, containing as its principal constituents a substance known as *globuline*, which very nearly resembles albumen, and the peculiar colouring matter of the blood, which is called *hæmatine*.

Beside these, the globules contain a little fatty matter and certain mineral constituents, especially the iron (which is associated in some unknown form with the colouring matter), the chlorides of sodium and potassium, and the phosphates of potash, soda, lime, and magnesia.

Though the quantities of these constituents are not invariable, even in the same individual, the following numbers may be taken as representing the average composition of these globules:—

1000 *parts of Blood Globules contain*—

Water,	688·00	Organic substances of unknown nature,	2·60
Globuline,	282·22	Mineral substances,*	8·12
Hæmatine,	16·75		
Fat,	2·31		

* Exclusive of the iron which is associated with the hæmatine.

The mineral substances consist of—

Potassium, ...	3·328	Oxygen, ...	0·667
Phosphoric acid, . . .	1·134	Phosphate of lime, . .	0·114
Sodium, ...	1·052	Phosphate of magnesia, .	0·073
Chlorine, ...	1·686	Sulphuric acid, . . .	0·066

Globuline is a substance very similar in its character and composition to albumen; it is found also in large proportion in the matter composing the crystalline lens of the eye.

The *hæmatine* or *hæmatosine* must be accounted the most important constituent of the blood globules, since it appears to be more intimately connected than any other with the functions discharged by the blood in nutrition and respiration.

In order to obtain it in the separate state, the blood globules are boiled with alcohol acidulated with sulphuric acid, and the red solution mixed with carbonate of ammonia, which separates the greater part of the globuline; the filtered liquid is evaporated to dryness, and all soluble matters are extracted by successive treatments with water, alcohol, and ether. By again dissolving the brown residue in alcohol containing ammonia, filtering, evaporating to dryness, and removing any soluble matter by water, a dark brown substance is obtained, which is supposed to be pure hæmatine, though no longer in the soluble state in which it existed in the blood. It is now dissolved only by alkalies or by acidulated alcohol.

In its chemical composition hæmatine is remarkable for the presence of iron, associated in a very intimate manner with carbon, hydrogen, nitrogen, and oxygen, so that it cannot be recognised by the ordinary tests. The formula which has been assigned to it is $C_{44}H_{44}N_6O_6Fe$, but it is rather doubtful whether it has been analysed in a perfectly pure state.

The most important chemical property of hæmatine is its behaviour with oxygen. It is well known that the blood issuing from an artery has a much brighter red colour than that drawn from a vein, and that when the latter is allowed to coagulate, the upper part of the clot, which is in contact with the air, is brighter than the lower part.

When the dark red blood drawn from a vein is shaken up with air or oxygen, a quantity of the latter is absorbed, and a nearly equal volume of carbonic acid is disengaged, the dark red colour being at the same time changed to the bright red characteristic of arterial blood. The carbonic acid exists already formed in the venous blood, and is given off if the blood is exposed under an exhausted receiver. The condition assumed by the oxygen when absorbed by the blood is not yet clearly understood, but it is generally allowed that the conversion of venous into arterial blood is due to the displacement of carbonic acid by oxygen.

The liquid in which the blood globules float is an alkaline solution containing albumen, fibrine, and saline matters in about the proportions here indicated.

1000 *parts of* Liquor Sanguinis *contain—*

Water, ...	902·90	Organic substances of unknown nature, . .	3·94
Albumen, ...	78·84	Mineral substances, . .	8·55
Fibrine, ...	4·05		
Fat, ...	1·72		

The mineral substances consist of—

Sodium,	3·341	Phosphoric acid,	0·191
Chlorine,	3·644	Sulphuric acid,	0·115
Potassium,	0·323	Phosphate of lime,	0·311
Oxygen,	0·403	Phosphate of magnesia,	0·222

The alkaline character of this liquid appears to be due to the presence of carbonate and phosphate of soda.

The *albumen* present in the serum of blood causes it to coagulate to a gelatinous mass when heated, this property being the distinctive feature of albumen. This substance may be obtained as a transparent yellow mass, resembling gum, and dissolving slowly in water, by evaporating either serum of blood or white of egg below 120° F.; but if the temperature be raised above that point, the albumen is coagulated, and cannot be redissolved in water unless heated with it under pressure.

Albumen, like caseine, has never been obtained perfectly free from saline matters, particularly the alkaline and earthy phosphates, and much difficulty attends the exact determination of its composition. The simplest formula which can be assigned to it is $C_{108}H_{169}N_{27}O_{34}S$.

It will be remembered that a substance identical with, or very closely resembling, albumen, and known as *vegetable albumen*, is found in those vegetable juices which are coagulated by heat.

Fibrine, as existing in blood, differs from all other animal substances by its tendency to spontaneous coagulation. When coagulated it exhibits characters very similar to those of coagulated albumen; but when separated from the freshly drawn blood by violent stirring, it forms elastic strings which dry into a yellow horny mass. Fibrine is one of the most important constituents of the animal frame, for all muscular flesh consists of this substance. The gluten found in the seeds of the cerealia bears a very close resemblance to fibrine, and is often called *vegetable fibrine*.

The same formula has been often assigned to fibrine as to albumen, and its complexity would explain its disposition to putrefy when removed from the influence of life. It does not appear quite certain that the fibrine dissolved in the blood is identical in composition with that of muscular fibre. Some analyses have shown that the muscular fibrine contains more oxygen than blood-fibrine, and this latter more than albumen, affording some ground for the belief that the blood-fibrine represents the transition state between the albumen of the serum and the muscular flesh into which it is eventually converted.

Albumen, fibrine, and caseine have been regarded by some chemists as compounds of the same primary substance (*proteine*) combined with different proportions of sulphur and phosphorus, the proteine being isolated by boiling the albuminous body with potash and precipitating the solution by an acid. The composition usually assigned to this substance is $C_{18}H_{27}N_4O_6$; but since it is neither crystallisable nor capable of conversion into vapour, there is no proof of its purity; and the great use which has been made of this substance by writers on animal chemistry is due to the apparent simplicity which it confers upon the relations existing between the numerous modifications of albumen, fibrine, and caseine, the ultimate formulæ of which present so high a degree of complexity.

In the substance of the brain there has been found a very remarkable crystalline substance, which has been termed *protagon*, and is a complex compound of carbon, hydrogen, nitrogen, oxygen, and perhaps phosphorus,

to which no probable formula has yet been assigned. It is very easily decomposed, even below 212°. Protagon is insoluble in water, but dissolves in hot alcohol and in acetic acid. When boiled with solution of baryta, it yields *phosphoglyceric acid*, and a strongly alkaline base *neurine*.

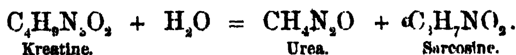
EGGS.—The shell of the egg contains about nine-tenths of its weight of carbonate of lime, associated with animal matter. The white of egg consists of albumen (about 12 per cent.), water (about 86 per cent.), and small quantities of soluble salts. It is alkaline, from the presence of a little soda. Raw white of egg has no smell of sulphuretted hydrogen, and does not blacken silver; but after boiling, both these properties are manifested, showing that it suffers some decomposition during coagulation. Yolk of egg contains a modification of albumen termed *vitelline*, and owes its colour to a yellow oil which may be extracted with ether, and contains phosphoric acid. The yolk of hens' eggs has about half the weight of the white, and commonly contains about half its weight of water, 16 per cent. of vitelline, 30 per cent. of fat, and 1·5 per cent. of saline matters.

434. FLESH.—The fibrine composing muscular flesh contains about three-fourths of its weight of water, a part of which is due to the blood contained in the vessels traversing it, and another part to the *juice of flesh*, which may be squeezed out of the chopped flesh. In this juice of flesh there are certain substances which appear to play a very important part in nutrition. The liquid is distinctly acid, which is remarkable when the alkaline character of the blood is considered, and contains phosphoric, lactic, and butyric acid, together with kreatine, inosite, and saline matters. By soaking minced flesh in cold water and well squeezing it in a cloth, a red fluid is obtained containing the juice of flesh mixed with a little blood. When the liquid is gently heated, the albumen of the blood and of the juice is coagulated in flakes stained with the colouring matter; the liquid filtered from these may be mixed with baryta water to precipitate the phosphoric acid; and after a second filtration, evaporated to a syrupy consistence and set aside, when beautiful colourless prismatic crystals are obtained, consisting of a feeble organic base called *kreatine*,* the composition of which is represented by the formula $C_4H_9N_3O_2.Aq$.

The quantity of this substance obtained from the flesh of different animals varies very considerably, that of fowls having been found hitherto most productive, and next that of fish. 1000 parts of the flesh of fowl furnished 3·2 parts of kreatine, 1000 parts of cod, 1·71 of kreatine, and 1000 of beef, 0·70 parts. Human flesh is said to contain a large proportion of kreatine.

When boiled with acids, kreatine loses the elements of water, and is converted into a powerful base called *kreatinine* ($C_4H_7N_3O$), which is also found in minute proportion, accompanied by kreatine, in the urine.

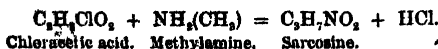
Boiled with alkalies, kreatine gains the elements of water, and furnishes two organic bases, *urea**(also found in urine), and *sarcosine* (σάρξ, flesh).†



$$\underset{\text{Kreatine.}}{C_4H_9N_3O_2} + H_2O = \underset{\text{Urea.}}{CH_4N_2O} + \underset{\text{Sarcosine.}}{C_3H_7NO_2}.$$

* From κρέας, flesh.

† Sarcosine has been obtained artificially by the action of chloracetic acid on methylamine;



$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Methylamine.}}{NH_2(CH_3)} = \underset{\text{Sarcosine.}}{C_3H_7NO_2} + HCl.$$

From the concentrated flesh-extract which has deposited the kreatine, there may be obtained, by careful treatment, crystals of a sweet substance called *inosite* or *sugar of flesh*, and having the composition $C_6H_{12}O_6.2Aq$. At a temperature below 212° F. it loses water, and has then the same composition as dry grape-sugar, $C_6H_{14}O_7$, with which, however, it is certainly not identical.

Inosite has been obtained in very minute proportion from flesh, but unripe beans are said to yield as much as 0·75 per cent. of this interesting sugar.

The saline constituents of the juice of flesh are chiefly phosphates of potash, magnesia, and lime, with a little chloride of sodium.

It is worthy of notice that potash is the predominant alkali in the juice of flesh, whilst soda predominates in the blood, especially in the serum.

According to Liebig, the acidity of the juice of flesh is chiefly due to the acid phosphate of potash, $K_2O.2H_2O.P_2O_5$, whilst the alkalinity of the blood is caused by the phosphate of soda, $2Na_2O.H_2O.P_2O_5$; and it has been suggested that the electric currents which have been traced in the muscular fibres are due to the mutual action between the acid juice of flesh and the alkaline blood, separated only by thin membranes from each other, and from the substance of the muscles and nerves.

The average composition of flesh may be represented as follows:—

Water,	78
Fibrine, vessels, nerves, cells, &c.,	17
Albumen,	2·5
Other constituents of the juice of flesh,	2·5
	100·0

Liebig's extract of meat is prepared by exhausting all the soluble matters from the flesh with cold water, separating the albumen by coagulation, and evaporating the liquid at a steam heat to a soft extract. It contains about half its weight of water, 40 per cent. of the organic constituents of the juice of flesh (albumen excepted), and 10 per cent. of saline matter.

Cooking of Meat.—A knowledge of the composition of the juice of flesh explains the practice adopted in boiling meat, of immersing it at once in boiling water, instead of placing it in cold water, which is afterwards raised to the boiling point. In the latter case, the water would soak into the meat, and remove the important nutritive matter contained in the juice; whilst, in the former, the albumen in the external layer of flesh is at once coagulated, and the water is prevented from penetrating to the interior. In making soup, of course, the opposite method should be followed, the meat being placed in cold water, the temperature of which is gradually raised, so that all the juice of flesh may be extracted, and the muscular fibre and vessels alone left.

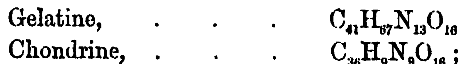
The object to be attained in the preparation of beef-tea, is the extraction of the whole of the soluble matters from the flesh, to effect which the meat should be minced as finely as possible, soaked for a short time in an equal weight of cold water, and slowly raised to the boiling point, at which it is maintained for a few minutes. The liquid strained from the residual fibrine contains all the constituents of the juice except the albumen, which has been coagulated.

When meat is roasted, the internal portions do not generally attain a sufficiently high temperature to coagulate the albumen of the juice, but the outside is heated far above 212° F.; so that the meat becomes impregnated to a greater extent with the melted fat, and some of the constituents of the juice in this part suffer a change, which gives rise to the peculiar flavour of roast meat. The brown sapid substance thus produced has been called *osmazome*,* but nothing is really known of its true nature.

In salting meat for the purpose of preserving it, a great deal of the juice of flesh oozes out, and a proportionate loss of nutritive matter is sustained.

435. *Gelatine.*—When portions of meat, containing cartilages (gristle) or tendons, are boiled for some time with water, the liquid so obtained sets to a jelly on cooling. This is due to the presence of *gelatine* or *chondrine*, or both—substances so nearly resembling each other, that they were long confounded under the name of gelatine. The difference in their origin is that gelatine is obtained by the action of water at a high temperature on skin, membrane, and bone,† whilst chondrine is obtained in the same way from the cartilages. In their properties there is very little difference, the most important being that a solution of chondrine is precipitated by acetic acid, by alum, and by acetate of lead, which do not precipitate gelatine.

In composition there is a considerable difference between gelatine and chondrine, the latter containing considerably more oxygen and less nitrogen. The simplest formulæ which have been assigned to them are—



Gelatine, . . . $C_{41}H_{67}N_{13}O_{16}$
Chondrine, . . . $C_{36}H_{9}N_{9}O_{16}$;

but they both contain phosphates of lime and magnesia in a very intimate state of association.

The characteristic properties of gelatine are the tendency of its solution to gelatinise on cooling, and the formation of an insoluble compound with tannic acid. The latter is the foundation of the art of tanning (p. 581), and the former is turned to account in the preparation of jelly, size, and glue. A solution containing only one per cent. of gelatine will set on cooling, though if it be repeatedly boiled it loses this property.

Isinglass is a very pure variety of gelatine prepared from the air bladder of fishes, especially of the sturgeon.

For the manufacture of *glue* the refuse and parings of hides are generally employed, after being cleansed from the hair and blood by steeping in lime water, and thoroughly exposed to the air for some days, so as to convert the lime into carbonate, and prevent the injurious effect of its alkaline character upon the gelatine. They are then boiled with water till the solution is found to gelatinise firmly on cooling, when it is run off into another vessel, where it is kept warm to allow the impurities to settle down, after which it is allowed to gelatinise in shallow wooden coolers. The jelly is cut up into slices, and dried upon nets hung up in a free current of air. Spring and autumn are usually selected for drying glue, since the summer heat would liquefy it, and frost would, of course, split it, and render it unfit for the market.

* From ὀσμή, odour; ζωμός, soup.

† The animal matter of bone appears to be isomeric with gelatine, and is called *osseine*.

Size is made in a similar manner, but finer skins are employed, and the drying is omitted, the size being used in the gelatinous state. The best size is made from parchment cuttings.

By the action of acids or alkalies upon gelatine, two crystalline organic bases may be obtained, known by the names of *glycocoll*, *glycocine*, or *sugar of gelatine* ($C_2H_5NO_2$), and *leucine* ($C_6H_{13}NO_2$).

It will be seen that glycocine is isomeric with nitrous ether ($C_2H_5.NO_2$), and leucine with the (at present unknown) nitrous ether of the caproic series. Leucine has been found in bullock's lungs and in calf's liver.

A large number of animal substances very nearly resemble gelatine in their composition; among these are hair, wool, nails, horns, and hoofs.

Hair contains, in addition to carbon, hydrogen, nitrogen, and oxygen, from 3 to 5 per cent. of sulphur.

Wool has sometimes to be separated from the cotton in worn-out mixed fabrics. The mixture is plunged into diluted hydrochloric acid, dried at 220° F., and submitted to the action of a machine (*devil*), which removes the cotton, rendered brittle by the action of the acid, in the form of dust, and leaves the wool fibres untouched. When the object is to save the cotton fibre, the fabric is exposed to high-pressure steam, which has no action upon cotton, but converts the wool into a brown matter easily removed by a beating machine, and sold, for manure, as *ulmate of ammonia*.

Silk is said to consist of three layers, the outermost consisting of gelatine, and soluble in water; the next of albumen, soluble in acetic acid on boiling; and the third of a nitrogenised substance called *sericine*, which is insoluble in water and acetic acid. Spider's threads appear to consist of this substance.

Sponge consists of a similar material, which has been called *fibroine*.

436. URINE.—The urine of animals is characterised by the presence of certain substances which are only met with in very minute quantities, if at all, in a state of health, in the other fluids of the body. The most important of these are an organic base called *urea*, *uric acid*, and *hippuric acid*.

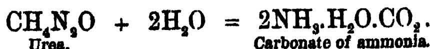
Urea.—When human urine is evaporated to about an eighth of its original bulk, and mixed with an equal volume of nitric acid, a semi-solid mass is formed consisting of pearly scales of nitrate of urea ($CH_4N_2O.HNO_3$). If these be washed with cold water, afterwards dissolved in boiling water, and treated with carbonate of baryta, the nitric acid combines with the baryta, and the carbonic acid having no tendency to combine with the urea, passes off, leaving the urea in solution—



$$\underbrace{2(CH_4N_2O.HNO_3)}_{\text{Nitrate of urea.}} + BaO.CO_2 = \underbrace{2CH_4N_2O}_{\text{Urea.}} + Ba2NO_3 + H_2O + CO_2.$$

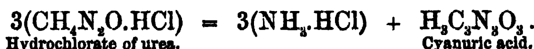
After filtering from the excess of carbonate of baryta, the liquid is evaporated on a water-bath, when a mixture of urea and nitrate of baryta is obtained, from which the urea may be extracted by hot alcohol. On evaporating the alcohol, beautiful prismatic crystals of urea are deposited. These crystals, when once separated from the urine in a pure state, may be preserved indefinitely even if dissolved in water; but the urea occurring in the urine is very soon decomposed, a putrefactive decomposition being excited by the *mucus*, a changeable substance somewhat resembling albumen, which collects in feathery clouds in the urine. The change-

which is thus induced in the urea results in its conversion into carbonate of ammonia—



$$\underset{\text{Urea.}}{CH_4N_2O} + 2H_2O = \underset{\text{Carbonate of ammonia.}}{2NH_3.H_2O.CO_2}.$$

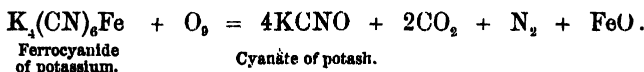
It is in consequence of this change that the urine so soon exhales an ammoniacal odour. In order to effect the same change in pure urea, it is necessary to heat it with water under high pressure. When urea is combined with hydrochloric acid, and the hydrochlorate is heated, it furnishes hydrochlorate of ammonia and cyanuric acid, according to the equation—



$$\underset{\text{Hydrochlorate of urea.}}{3(CH_4N_2O.HCl)} = 3(NH_3.HCl) + \underset{\text{Cyanuric acid.}}{H_3C_3N_3O_3}.$$

When cyanuric acid is distilled, it yields 3 molecules of hydrated cyanic acid (HCNO), and the connexion thus established between urea and the cyanogen series becomes intelligible when we see that this base is isomeric with cyanate of ammonia ($NH_3.HCNO$). In fact, by combining hydrated cyanic acid with ammonia, and evaporating the solution, no cyanate of ammonia, but simply urea, is obtained.

Upon this has been founded a process for obtaining urea artificially, which has attracted a great deal of attention as one of the earliest examples of the production in the laboratory, of a complex substance formed in the animal body. For the artificial production of urea, 56 parts of well-dried ferrocyanide of potassium are intimately mixed with 28 parts of dried binoxide of manganese, and the mixture heated to dull redness in an iron dish, and stirred until it ceases to smoulder. The oxygen supplied by the binoxide of manganese converts the potassium and part of the cyanogen of the ferrocyanide into cyanate of potash, the remainder of the cyanogen being burnt, and the iron converted into oxide—



$$\underset{\text{Ferrocyanide of potassium.}}{K_4(CN)_6Fe} + O_9 = \underset{\text{Cyanate of potash.}}{4KCNO} + 2CO_2 + N_2 + FeO.$$

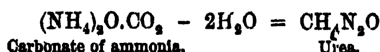
On treating the residue with cold water, the cyanate of potash is dissolved out, and after the insoluble portion has subsided, the liquid may be poured off, and 41 parts of sulphate of ammonia dissolved in it. Sulphate of potash and cyanate of ammonia are thus formed—



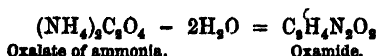
$$2KCNO + 2NH_3.H_2O.SO_3 = K_2O.SO_3 + 2(NH_3.HCNO);$$

and if the solution be evaporated to dryness (on a water-bath) the latter salt is transformed into urea, which may be separated from the sulphate of potash by alcohol, which dissolves the urea only.

437. The true constitution of urea has been the subject of much discussion among chemists. The circumstance that, under certain conditions, this base assimilates the elements of water and is converted into carbonate of ammonia, has led to the opinion that urea should be classed among the amides (p. 540), when it would be represented as derived from carbonate of ammonia $(NH_4)_2O.CO_2$ by the loss of water, just as oxamide is derived from oxalate of ammonia—



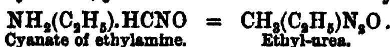
$$\underset{\text{Carbonate of ammonia.}}{(NH_4)_2O.CO_2} - 2H_2O = \underset{\text{Urea.}}{CH_4N_2O}$$



$$\underset{\text{Oxalate of ammonia.}}{(NH_4)_2C_2O_4} - 2H_2O = \underset{\text{Oxamide.}}{C_2H_4N_2O_2}$$

The question naturally presents itself, whether the various bases formed by substitution from ammonia (p. 530) would furnish corresponding ureas when acted

upon by cyanic acid. This has been actually found to be the case; ethylamine $NH_2(C_2H_5)$, for example, acting upon cyanic acid, yields ethyl-urea, which is isomeric with the cyanate of ethylamine, just as urea is isomeric with cyanate of ammonia.

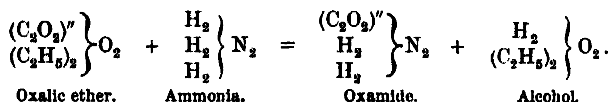


It is evident that if urea be derived from a double molecule of ammonia by the substitution of CO for H_2, then ethyl-urea will be derived in a similar manner from a double molecule of ethylamine.

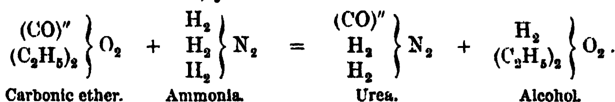


In this case it will be observed that the diatomic group CO, is substituted for one atom of the hydrogen, and for one of its representative, ethyle.

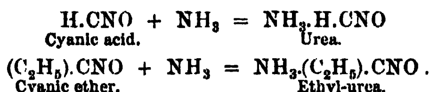
It will be remembered that the amides can be obtained by the action of ammonia upon the corresponding ethers; thus oxalic ether treated with ammonia gives oxamide, and the conversion may be intelligibly represented thus—



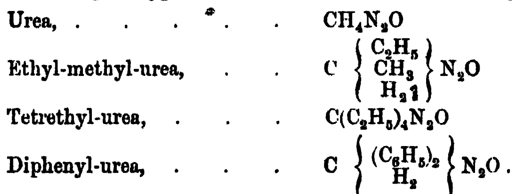
In a similar manner, carbonic ether, when heated in a sealed tube with an alcoholic solution of ammonia, yields urea and alcohol—



When cyanic ether ($C_2H_5.CNO$) is acted on by ammonia, it yields ethyl-urea, the action being precisely parallel to that of ammonia upon cyanic acid—

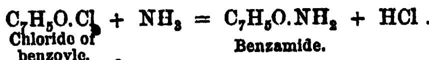


Many other compound ureas of this description have been obtained, in which the hydrogen is partly or entirely replaced by the alcohol radicals. The relation existing between these and their prototype, urea, will be seen in the following examples:—

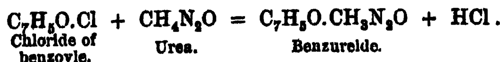


The supposition that urea is really constituted upon the ammonia type derives some confirmation from the circumstance, that a number of substances have been obtained which bear the same relation to urea as the amides do to ammonia. They are, therefore, sometimes styled *ureides*, and sometimes compound ureas, in which a negative or acid radical occupies the place of a part of the hydrogen. In illustration of the mode of formation of the bodies of this class, the production of benzureide or benzoyl-urea may be referred to.

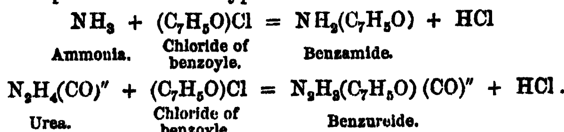
When ammonia acts upon chloride of benzoyle, it yields benzamide and hydrochloric acid—



If urea be substituted for the ammonia, benzureide and hydrochloric acid are formed—



Both reactions become much more intelligible if urea and its derivatives be allowed to be composed upon the ammonia type—



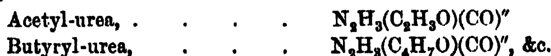
$$NH_3 + (C_7H_5O)Cl = NH_2(C_7H_5O) + HCl$$

Ammonia. Chloride of benzoyle. Benzamide.

$$N_2H_4(CO)'' + (C_7H_5O)Cl = N_2H_3(C_7H_5O)(CO)'' + HCl.$$

Urea. Chloride of benzoyle. Benzureide.

By similar processes there have been obtained—



Acetyl-urea, ... $N_2H_3(C_2H_3O)(CO)''$
Butyryl-urea, ... $N_2H_3(C_4H_7O)(CO)''$, &c.

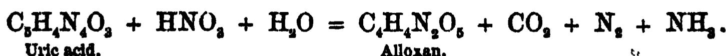
438. *Uric acid.*—When human urine is acidified with hydrochloric acid and allowed to stand for some time, it deposits minute hard red grains, consisting of *uric acid* ($C_5H_4N_4O_3$) tinged with the urinary colouring matter. In urine the acid is present as urate of soda and urate of ammonia, which are often deposited from urine in slight derangements of the system, when they are present in excess, these salts being very much more soluble in warm water than in cold. Since uric acid and its salts are very common ingredients of calculi, this acid is sometimes called lithic acid (λίθος, a stone).

As the quantity of uric acid in human urine does not exceed 1 grain in 1000, recourse is had to other sources for the preparation of this acid, which is now extensively used for the preparation of the *murexide* employed in calico-printing.

The excrements of the boa-constrictor and of birds, which consist almost entirely of acid urate of ammonia, and *guano*, which has been formed by the partial decomposition of the excrements of sea-birds, are excellent sources of uric acid. The separation of the uric acid from acid urate of ammonia is easily effected by dissolving it in solution of potash, filtering, and adding hydrochloric acid, when the uric acid, which requires 10,000 parts of cold water to dissolve it, is precipitated as a white crystalline powder.

When a solution of potash is saturated with uric acid in the cold, and boiled down out of contact with air, small needle-like crystals are deposited, having the composition $K_2.C_5H_2N_4O_3$, and if this be dissolved in water, and carbonic acid be passed through the solution, half the potassium is removed as carbonate, and a granular precipitate of acid urate of potash, $K.H.C_5H_2N_4O_3$ is deposited. Uric acid, therefore, is a dibasic acid, and the formula of the acid itself ($C_5H_4N_4O_3$) should be written $H_2C_5H_2N_4O_3$.

When uric acid is added by degrees to strong nitric acid, it dissolves with effervescence and evolution of heat; the solution, on cooling, deposits octahedral crystals of a substance called *alloxan* ($C_4H_4N_2O_5$), which may be represented as formed by the oxidation of the uric acid according to the following equation—



$$C_5H_4N_4O_3 + HNO_3 + H_2O = C_4H_4N_2O_5 + CO_2 + N_2 + NH_3.$$

Uric acid. Alloxan.

Alloxan has the curious property of staining the fingers of a beautiful pink colour, and its solution gives an intense purple colour with sulphate of iron.

A connexion is established, by means of alloxan, between uric acid and urea, which becomes important, because these two bodies, accompanied

by a small quantity of alloxan, are always found together in the urine. Alloxan appears to be the intermediate stage in the conversion of uric acid into urea by oxidation, for if a solution of alloxan be boiled with peroxide of lead (PbO_2) carbonic acid is evolved, and the alloxan is converted into urea by oxidation—



$$\underset{\text{Alloxan.}}{C_4H_4N_2O_5} + 2PbO_2 = \underset{\text{Urea.}}{CH_4N_2O} = 3CO_2 + 2PbO.$$

When sulphuretted hydrogen is passed through a solution of alloxan, the liquid is troubled by the separation of sulphur, and deposits prismatic crystals of *alloxantine* ($C_8H_4N_4O_7$)—



$$\underset{\text{Alloxan.}}{2C_4H_4N_2O_5} + H_2S = \underset{\text{Alloxantine.}}{C_8H_4N_4O_7} + 3H_2O + S.$$

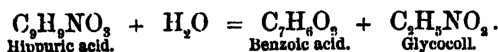
If 4 grains of alloxantine and 7 grains of crystallised alloxan be dissolved in hot water, and 80 grains of a cold saturated solution of carbonate of ammonia added, the carbonic acid is disengaged with effervescence, and the liquid assumes a brilliant purple colour, depositing as it cools splendid crystals, which have a red colour by transmitted light, and reflect a play of green and gold, like the wing of the sun-beetle.

This magnificent substance is known as *murexide*, and has the formula $C_8H_8N_6O_6$.

The beautiful colour of murexide has been applied to dyeing and calico-printing, being prepared for that purpose from the uric acid furnished by guano.

439. *Hippuric acid.*—Another acid peculiar to the urine, and found in very minute quantity in human urine, is hippuric acid ($C_9H_9NO_3$), so named because it occurs in far larger quantity in the urine of horses (*ἵππος, a horse*) and cows, the cow's urine yielding more than 1 per cent. of the acid. It is generally prepared from cow's urine by evaporating it to about an eighth of its bulk, and adding an excess of hydrochloric acid. On standing, long prismatic needles of hippuric acid are deposited. It is remarkable that this acid can be obtained only from the urine of stall-fed cows or of horses kept at rest, for if the animals are actively exercised, the above treatment educes benzoic acid ($C_7H_6O_2$) in place of hippuric. Again, only the fresh urine yields hippuric acid, for after putrefaction, only benzoic acid can be obtained from it. Conversely, if benzoic acid be administered to an animal, it makes its appearance as hippuric acid in the urine.

The relation between these two acids becomes evident when hippuric acid is boiled for some time with strong hydrochloric acid; on cooling, the solution deposits crystals of benzoic acid, and if the liquid separated from these be evaporated, neutralised with ammonia, and mixed with alcohol, crystals of glycocoll (p. 609) are obtained.



$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + H_2O = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Glycocoll.}}{C_2H_5NO_2}.$$

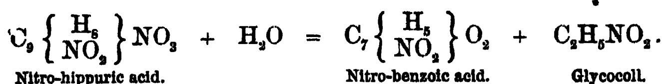
This result has been confirmed synthetically by acting upon the compound resulting from the action of glycocoll on oxide of zinc, with chloride of benzoyle (p. 470), when hippuric acid is reproduced.



$$\underset{\text{Zinc-glycocoll.}}{Zn.2C_2H_4NO_2} + \underset{\text{Chloride of benzoyle.}}{2(C_7H_5O.Cl)} = ZnCl_2 + \underset{\text{Hippuric acid.}}{2C_9H_9NO_3}.$$

Hippuric acid, therefore, may be represented as *benzoyle-glycocoll*,

$C_2H_4(C_7H_5O)NO_2$. A very interesting illustration of the doctrine of substitution is connected with these acids. By acting upon hippuric acid with nitric and sulphuric acids, it is converted into nitro-hippuric acid by the substitution of NO_2 for one atom of its hydrogen, and if this acid be boiled with hydrochloric acid, it yields nitrobenzoic acid, just as hippuric yields benzoic acid—



$$C_9\left\{\begin{matrix}H_8\\NO_2\end{matrix}\right\}NO_3 + H_2O = C_7\left\{\begin{matrix}H_5\\NO_2\end{matrix}\right\}O_2 + C_2H_5NO_2.$$

Nitro-hippuric acid. Nitro-benzoic acid. Glycocoll.

In contact with bases, hippuric acid forms salts of the general formula $M,C_9H_8NO_3$, so that the acid itself should be written as $HC_9H_8NO_3$.

In addition to the organic substances which have been already mentioned as occurring in the urine (urea, uric acid, mucus, hippuric acid, kreatinine), it always contains a large proportion of alkaline and earthy salts, especially of chloride of sodium, phosphate and sulphate of potash, and phosphates of lime, magnesia, and ammonia.

The average composition of human urine may be thus stated—

Water,	956·80
Urea,	14·23
Uric acid,	0·37
Mucus,	0·16
Hippuric acid, kreatinine, ammonia, colouring matter, and unknown organic matters,	15·03
Chloride of sodium,	7·22
Phosphoric acid,	2·12
Potash,	1·93
Sulphuric acid,	1·70
Lime,	0·21
Magnesia,	0·12
Soda,	0·05
	999·94

CHEMISTRY OF VEGETATION.

440. The ultimate elements of plants, that is, the substances with which plants must be supplied in one form or other, to sustain their growth, are carbon, hydrogen, nitrogen, oxygen, sulphur, phosphorus, chlorine, silicon, potassium, sodium, calcium, magnesium, iron, manganese.

Of these, the carbon, hydrogen, nitrogen, oxygen, sulphur, and phosphorus are grouped together to form the various organic compounds furnished by plants, the remaining elements being arranged generally in the following forms:—

Chlorides of potassium and sodium,
Sulphate of lime,
Silicates of potash and soda,
Phosphates of iron (manganese?), lime, magnesia, and ammonia,
Compounds of potash, soda, and lime, with vegetable acids.

Plants are capable of receiving food either in the form of gas through the instrumentality of their leaves, or in solution by their roots.

The carbon, which is their most important constituent as regards quantity, is taken up in the form of carbonic acid by both these organs of the plant. This carbonic acid is derived either from the surrounding atmo-

sphere, or from the decay of the organic matters contained in the soil which surrounds the roots of the plant.

The hydrogen is derived partly from water and partly from the ammonia which is carried down to the roots of the plant by rain, or is evolved in the putrefaction and decay of the nitrogenised organic matters of the soil. The ammonia also forms one great source of the nitrogen in plants, another being the nitric or nitrous acid, which is either brought down by the rain, or formed within the soil by the nitrification of the ammonia (p. 129). As to the oxygen, it is obtained both from the carbonic acid and water, which contain this element in larger proportion than is ever present in any vegetable product.

The sulphur and phosphorus contained in the organic parts of the plant appear to be chiefly derived from the sulphates and phosphates of the soil.

The chlorine, silicon, and the metals, are derived from the mineral constituents of the soil.

It is not difficult to imagine the course of formation of a fertile soil from a primary rock (of granite, for example) under the influence of the atmosphere and rain, exerted through a very long period.

It will be remembered that granite consists essentially of quartz (silica), feldspar (silicate of alumina and potash or soda), and mica (silicates of alumina, iron, potash, and magnesia); in addition to these there may always be found in granite minute quantities of phosphate of lime, of sulphates, of chlorides, and of manganese.

By the disintegration of such a rock under the action of air and moisture (p. 285), a soil will be formed containing the various *mineral* substances required for the food of the plant. If now, upon the thin layer of soil thus formed over the face of the rock, some seeds of the lower orders of plants, the lichens, for instance, be deposited, they will grow and fructify, deriving their carbon, hydrogen, nitrogen, and oxygen from the air and rain, and their mineral constituents from the soil. The death of these lichens would add new elements of fertility to the soil, in the shape of the food which they had condensed from the air, and of the saline ingredients which had been converted within their organisations into forms better suited to sustain the higher orders of plants. Given, then, the seeds of a higher vegetation, a similar process may be supposed to take place, and at length animals would be attracted to the spot by the prospect of vegetable food, and by transporting to it elements which they had derived from other sources, would eventually confer upon it the highest fertility. The soil then coming under tillage, the crops raised upon it are consumed by animals and removed to a distance, so that the mineral food contained in the soil is by degrees exhausted, and unless it is restored the soil becomes barren.

To restore its fertility is the object of manuring, which consists in adding to the soil some substance which shall itself serve directly as food for the plant, or shall so modify, by chemical action, some material already present in the soil, as to convert it into a state in which the plant may take advantage of it.

As examples of substances which are added as direct food for plants, may be enumerated:—

(1.) The ashes of peat, turf, coal, &c., which furnish the mineral substances originally obtained from the soil by the vegetables from which these materials were formed.

(2.) Gypsum, or sulphate of lime, and sulphate of magnesia, which appear to be valuable not only as sources of sulphur, calcium, and magnesium, but because they are capable of decomposing the carbonate of ammonia, which is either brought down by rain or evolved by putrefaction in the soil, and of converting it into sulphate of ammonia which is retained in the soil, whereas the carbonate, being a volatile salt, would be again exhaled into the air and lost to the plants.

(3.) Phosphate of lime, or bone-ash, which is most commonly converted into the soluble superphosphate of lime (p. 224) by treatment with sulphuric acid, before being employed as a manure.

(4.) Chloride of sodium, or common salt, serves as a source of sodium, for in contact with the carbonate of lime, which is found in all fertile soils, it is partly converted into carbonate of soda, which may in turn be converted into silicate of soda, or any other salt of that alkali necessary to the growth of the plant.

(5.) Nitrate of soda (Peruvian nitre) is held to be of great service in some cases, as yielding both soda and nitrogen in a form serviceable to the plant.

(6.) The silicates of potash and soda, which are especially useful to crops which, like the cereals, contain a considerable proportion of silica in their stems; since, although that substance is contained in abundance in all soils, it is not available for the plant unless converted into a soluble state by combination with an alkali.

(7.) Sulphate of ammonia (derived from the gas-works) is, of course, useful both for its sulphuric acid and ammonia.

(8.) Plants, or parts of plants, ploughed into a soil, would obviously furnish food for other plants by their gradual putrefaction and decay.

(9.) Bones, which furnish carbonic acid and ammonia by the putrefaction of their gelatinous matter, as well as a large supply of phosphate of lime.

(10.) Urine, yielding much carbonate of ammonia by the decomposition of its urea and uric acid, and an abundance of the phosphates and other saline matters required by the plant.

(11.) Solid excrements of various animals, containing the insoluble salts (especially phosphates) of the animal's food, as well as easily putrescible organic matters yielding much ammonia and sulphuretted hydrogen.

(12.) Guano, the dung of carnivorous sea-birds, which owes its very high value partly to the large proportion of urate of ammonia and other nitrogenised organic substances which it contains, and partly to the presence of phosphates and salts of the alkalies.

(13.) Soot, which appears to act chiefly by virtue of the salts of ammonia derived from the destructive distillation of the coal.

The chief substance employed for acting chemically upon the constituents of the soil, so as to render them more serviceable to the plant, is lime, which modifies in a very important manner both the organic and mineral portions of the soil. Its action upon the former consists in promoting its decay, and the conversion of its elements into those forms, viz., carbonic acid, water, ammonia, and nitric acid, in which they may be of service to the plant. Upon the inorganic constituents of the soil lime acts by assisting the decomposition of minerals, particularly of those which contain the alkalies (such as feldspar), and thus converting them into soluble forms.

In some cases fertility is restored to an apparently exhausted soil, with-

out the addition of manure, by allowing it to lie fallow for a time, so that, under the influence of the air and moisture, such chemical changes may take place in it as will again replenish it with food available for the crops. It is not even necessary in all cases that the soil should be altogether released from cultivation; for even though it may refuse to feed any longer one particular crop, it may furnish an excellent crop of a different description, and, which is more remarkable, it may, after growing two or three different crops, be found to have regained its power of nourishing the very crop for which it was before exhausted. Experience of this has led to the adoption of the system of *rotation of crops*, by which a soil is made to yield, for example, a crop of barley, and then successive crops of grass, beans, turnips, and barley again.

The possibility of this rotation is partly accounted for by the difference in the mineral food removed from the soil by different crops; thus turnips require much of the alkalies and lime; wheat, much alkali and silica; barley, much lime and silica; and clover, much lime, so that the soil which had been exhausted for wheat, because it no longer contained enough soluble silica, might still yield sufficient alkali and lime to a crop of turnips, and when the alkali was exhausted, might furnish enough lime to a crop of clover, after which, in consequence of the chemical changes allowed by lapse of time in the soil, more of the original minerals composing it might have been decomposed and rendered available for a fresh wheat crop.

Another explanation of the benefit of systems of rotation may be given in those cases in which the débris of the preceding crop are allowed to remain on the land. Some plants, extending their roots more deeply into the soil, avail themselves of mineral food which is beyond the reach of plants furnished with shorter roots, and when the refuse of the former plants is ploughed into the land, the surface is enriched with the food collected from the sub-soil.

Our knowledge of the chemical operations taking place in the plant, and resulting in the elaboration of the great variety of vegetable products, is very slight indeed. We appear to have sufficient evidence that sugar and starch, for example, are constructed in the plant from carbonic acid and water, that gluten results from the mutual action of the same compounds, together with ammonia, or nitric acid, and certain sulphates and phosphates, but what the intermediate steps in this conversion may be we are not in a position even to hazard a guess.

All seeds contain starch, gluten, or some similar nitrogenised substance (legumine, for example), together with mineral matters, these being provided for the nourishment of the young plant until its organs are sufficiently developed to enable it to procure its own food from the air or from the soil.

During the process of germination, the seed absorbs oxygen and evolves carbonic acid, and since the albuminous constituent is the most mutable substance present, it is probably this which undergoes oxidation, and excites the conversion of the insoluble starch into soluble sugar. At this stage the seed requires, as is well known, a fair supply of water, the elements of which are required for the conversion of the starch ($C_6H_{10}O_5$) into sugar ($C_6H_{12}O_6$); water is also required to dissolve the sugar as well as the altered albuminous matter and the mineral salts, in order to form the sap of the embryo plant. These constituents of the sap, directed by the

mysterious vital energy in the seed, build up the root, which extends itself in search of nourishment down into the soil, and the leaves, which discharge a similar function with respect to the air. As soon as the leaves are developed, the plant becomes able to decompose carbonic acid, water, and ammonia, to provide the organic components of its sap. Some part of these changes at least appears to take place in the leaves of the plant, from which, during the day-time, oxygen (together with a little nitrogen) is continually evolved. The leaves have been compared to the lungs of animals, the functions of which they reciprocate, for whilst, in the lungs of animals, an absorption of oxygen and an evolution of carbonic acid is observed, in the leaves of plants, it is the carbonic acid which is absorbed and oxygen is disengaged.

In the dark, plants exhale carbonic acid, but in much smaller quantity than they decompose in the light.

That oxygen must be evolved, if plants construct their carbonaceous compounds from carbonic acid and water, is obvious on reflecting that all these compounds contain less oxygen, in proportion to their carbon and hydrogen, than is contained in carbonic acid and water.

Thus, we may conceive the formation of all the compounds of carbon and hydrogen, or of those elements with oxygen, which are met with in plants, by the concurrence, in various proportions, of carbonic acid and water, and the separation of the whole or a part of their oxygen.

To take an example; cellulose ($C_6H_{10}O_5$) would result from the coalition of 6 mols. of carbonic acid and 5 mols. of water, with separation of 12 atoms of oxygen. Again, malic acid, $C_4H_6O_5$, would require 4 mols. of carbonic acid and 3 mols. of water, whilst 6 atoms of oxygen would be set free.

It is equally easy to represent the formation of nitrogenised compounds from carbonic acid, water, and ammonia, with separation of oxygen, for the nitrogen in all such compounds is present in so small a number of equivalents, relatively to the carbon and hydrogen, that the amount of oxygen separated from the carbonic acid and water would always far more than suffice to convert the whole of the hydrogen of the ammonia into water, even if this hydrogen did not itself take part in the formation of the compound. Suppose, for instance, that the formation of quinine is to be accounted for—



$$20CO_2 + 9H_2O + 2NH_3 = \underset{\text{Quinine.}}{C_{20}H_{24}N_2O_2} + O_{47}.$$

If sulphur be a constituent of the vegetable compound to be formed, it is conceivable that the sulphuric acid derived from the sulphates present in the soil should co-operate with the carbonic acid, water, and ammonia.

If the composition of gluten be correctly represented by the formula $C_{108}H_{169}N_{27}O_{34}S$, the equation explaining its formation from the above constituents of the food of the plant would be written—



$$108CO_2 + 44H_2O + 27NH_3 + SO_3 = C_{108}H_{169}N_{27}O_{34}S + O_{229}.$$

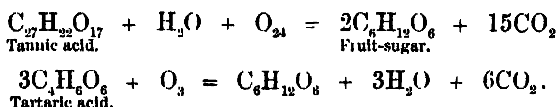
The chemical tendency of vegetables, therefore, is to reduce to a lower state of oxidation the substances presented in their food, whilst animals exhibit a reciprocal tendency to oxidise the materials on which they feed.

With respect to the last stage in the existence of the plant, the ripening

of the fruit, we know a little more concerning the chemical changes which it involves.

Most fruits, in their unripe condition, contain cellulose, starch, and some one or more vegetable acids, such as malic, citric, tartaric, and tannic, the latter being almost invariably present, and causing the peculiar roughness and astringency of the unripe fruit. The *characteristic* constituent of unripe fruits, however, is *pectose*, a compound of carbon, hydrogen, and oxygen, the composition of which has not been exactly determined. Pectose is quite insoluble in water, but during the ripening of the fruit it undergoes a change induced by the vegetable acids, and is converted into *pectine* ($C_{32}H_{40}O_{28}$), which is capable of dissolving in water, and yields a viscous solution. As the maturation proceeds, the pectine itself is transformed into *pectic acid* ($C_{16}H_{22}O_{15}$), and *pectosic acid* ($C_{32}H_{46}O_{31}$), which are soluble in boiling water, yielding solutions which gelatinise on cooling. It is from the presence of these acids, therefore, that many ripe fruits are so easily convertible into jellies.

Whilst the fruit remains green, its relation to the atmosphere appears to be the same as that of the leaves, for it absorbs carbonic acid, and evolves oxygen; but when it fairly begins to ripen, oxygen is absorbed from the air, and carbonic acid is evolved, whilst the starch and cellulose are converted into sugar, under the influence of the vegetable acids (p. 491), and the fruit becomes sweet. It has been already seen that the conversion of starch and cellulose ($C_6H_{10}O_5$) into sugar ($C_6H_{12}O_6$) would simply require the assimilation of the elements of water, so that the absorption of oxygen and evolution of carbonic acid are probably necessary for the conversion of the tannic and other acids into sugar. For example—



$$\underset{\text{Tannic acid.}}{C_{27}H_{22}O_{17}} + H_2O + O_{24} = \underset{\text{Fruit-sugar.}}{2C_6H_{12}O_6} + 15CO_2$$

$$\underset{\text{Tartaric acid.}}{3C_4H_6O_6} + O_3 = C_6H_{12}O_6 + 3H_2O + 6CO_2.$$

When the sugar has reached the maximum, the ripening is completed; and if the fruit be kept longer, the oxidation takes the form of ordinary decay.

The scheme of natural chemistry would not be complete unless provision were made for the restoration of the constituents of plants, after death, to the atmosphere and soil, where they might afford food to new generations of plants. Accordingly, very shortly after the death of a plant, if sufficient moisture be present, the changeable nitrogenised (albuminous) constituents begin to putrefy, and chemical motion being thus excited, is communicated to the other parts of the plant, under the form of decay, so that the plant is slowly consumed by the atmospheric oxygen, its carbon being reconverted into carbonic acid, its hydrogen into water, and its nitrogen into ammonia, these substances being then transported in the atmosphere to living plants which need them, while the mineral constituents of the dead plant are washed into the soil by the rain.

Moist wood is slowly converted by decay into a brown substance, which has been called *humus*, and forms the chief part of the organic matter in soils. Alkalies dissolve this substance, and on the addition of an acid to the brown solution, a brown precipitate is obtained, which is said to contain *humic*, *ulmic*, and *geic* acids, but these substances do not crystallise, and their existence as definite acids appears to be somewhat doubtful. Two other acids of a similar kind, *crenic* and *apocrenic acids*

(κρήνη, a well), have been obtained from the same source, and are also found occasionally in mineral waters.

When it is desired to preserve wood from decay, it is impregnated with some substance which shall form an unchangeable compound with the albuminous constituents of the sap. Kreasote (p. 455) and corrosive sublimate (*kyanising*) are occasionally used for this purpose, the wood being made to imbibe a diluted solution of the preservative, either by being soaked in it or under pressure.

In Boucherie's process for preserving wood, the natural ascending force of the sap is ingeniously turned to account in drawing up the preservative solution. A large incision being made around the lower part of the trunk of the growing tree, a trough of clay is built up around it, and filled with a weak solution of sulphate of copper, acetate of iron, or chloride of calcium. Even after the tree has been felled, it may be made to imbibe the preserving solution whilst in a horizontal position, by enclosing the base of the trunk in an impermeable bag supplied with the liquid from a reservoir. The impregnation of the wood with such solutions not only prevents chemical decay, but renders it less liable to the attacks of insects and the growth of fungi.

NUTRITION OF ANIMALS.

441. Between the chemistry of vegetable and that of animal life there is this fundamental distinction, that the former is eminently constructive, and the latter destructive. The plant supplied with compounds of the simplest kind—carbonic acid, water, and ammonia—constructs such complex substances as albumen and sugar; whilst the animal, incapable of deriving sustenance from the simpler compounds, being fed with those of a more complex character, converts them eventually, for the most part, into the very materials with which the constructive work of the plant commenced. It is indeed true, that some of the substances deposited in the animal frame, such as fibrine and gelatinous matter, rival in complexity many of the products of vegetable life; but for the elaboration of these substances, the animal must receive food somewhat approaching them in chemical composition. It is to this nearer resemblance between the food of animals and the proximate constituents of their frames, that we may partly ascribe the greater extent of our knowledge on the subject of the nutrition of animals, which is, however, far from being complete.

The *ultimate* elements contained in the animal body are the same as those of the vegetable, but the *proximate* constituents are far more numerous and varied.

The bones containing the phosphates and carbonates of lime and magnesia, together with gelatinous matter, require that the animal should be supplied with food which, like bread, contains abundance of phosphates, as well as the nitrogenised matter (gluten) from which the gelatinous substance may be formed. In milk, the food of the young animal, we have also the necessary phosphates, whilst the caseine affords the supply of nitrogenous matters.

Muscular flesh finds, in the gluten of bread and the caseine of milk, the nitrogenised constituent from which its fibrine might be formed with even less transformation than is required for the gelatinous matter of bone, since the composition of fibrine, gluten, and caseine is very similar.

The albumen and fibrine of the blood have also their counterparts in the gluten and caseine of bread and milk, whilst all the salts of the blood may be found in either of these articles of food.

Bread and milk, therefore, may be taken as excellent representatives of the food necessary for animals, and the same constituents are received in their flesh diet by animals which are purely carnivorous, but in a higher stage of preparation.

It is natural to suppose that those parts of the frame which contain no nitrogen should be supplied by those constituents of the food which are free from that element, such as the starch in bread and the sugar and fat in milk.

Before the food can be turned to account for the sustenance of the body, it must undergo *digestion*, that is, must be either dissolved or otherwise reduced to such a form that it can be absorbed by the blood, which it accompanies into the lungs to undergo the process of *respiration*, and thus to become fitted to serve for the *nutrition* of the various organs of the body, since these have to be continually repaired at the expense of the constituents of the blood.

The first step towards the digestion of the food is its disintegration, effected by the teeth with the aid of the *saliva*, by which it should be reduced to a pulpy mass. The saliva is an alkaline fluid characterised by the presence of a peculiar albuminous substance called *ptyaline* (πτύω, *to spit*), which easily putrefies. The action of saliva in mastication is doubtless in great part a mechanical one, but it is possible that its alkalinity assists the process chemically, by partly emulsifying the fatty portions of the food. The liability of ptyaline to putrefaction favours the supposition that it may act in some way as a ferment in promoting the digestion.

This disintegration of the food is of course materially assisted by the cooking to which it has been previously subjected, the hard and fibrous portions having been thereby softened.

The food now passes to the stomach, in which it remains for some time, at the temperature of the body (98° F.), in contact with the *gastric juice*, the chief chemical agent in the digestive process.

The gastric juice, which is secreted by the lining membrane of the stomach, is an acid liquid, containing hydrochloric and lactic acids. It is characterised by the presence of a peculiar substance belonging to the albuminous class of bodies, which is called *pepsine* (πέπτω, to digest), and possesses the remarkable power of enabling dilute acids, by its mere presence, to dissolve such substances as fibrine and coagulated albumen, which would resist the action of the acid alone for a great length of time.

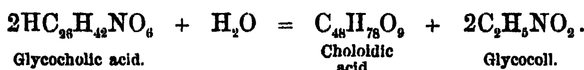
An imitation of the gastric juice may be made by digesting the mucous membrane of the stomach for some hours in warm very dilute hydrochloric acid. The acid liquid thus obtained is capable of dissolving meat, curd, &c., if it be maintained at the temperature of the body. The pepsine prepared from the stomach of the pig and other animals is sometimes administered medicinally in order to assist digestion.

The principal change which the food suffers by the action of the gastric juice is the conversion of the fibrinous and albuminous constituents into soluble forms; the starch is also partly converted into dextrine and sugar, but the fatty constituents are unchanged.

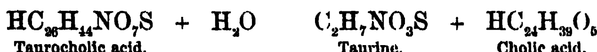
The food which has thus been partially digested in the stomach is called by physiologists *chyme*, and passes thence into the commencement of the

intestines (the *duodenum*), where it is subjected to the action of two more chemical agents, the *bile* and the *pancreatic juice*.

Bile consists essentially of a solution of two salts known as glycocholate and taurocholate of soda. Both glycocholic and taurocholic acids are resinous, and do not neutralise the alkali, so that the bile has a strong alkaline character. Another characteristic feature of this secretion is the large proportion of carbon which it contains. *Glycocholic acid* has the composition $HC_{26}H_{42}NO_6$, and contains therefore 67 per cent. of carbon, whilst *taurocholic acid*, $HC_{26}H_{44}NO_7S$, contains 61 per cent. The names of these acids have reference to the circumstance that they furnish respectively glycocoll and taurine, together with two new acids free from nitrogen, when they are boiled with dilute hydrochloric acid—



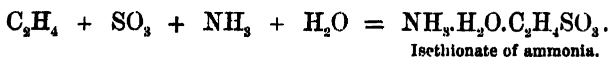
$$\underset{\text{Glycocholic acid.}}{2HC_{26}H_{42}NO_6} + H_2O = \underset{\text{Choloidic acid.}}{C_{48}H_{78}O_9} + \underset{\text{Glycocoll.}}{2C_2H_5NO_2}.$$



$$\underset{\text{Taurocholic acid.}}{HC_{26}H_{44}NO_7S} + H_2O \quad \underset{\text{Taurine.}}{C_2H_7NO_3S} + \underset{\text{Cholic acid.}}{HC_{24}H_{39}O_5}$$

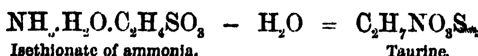
Taurine forms colourless crystals of great beauty, and is remarkable for the large proportion (above 25 per cent.) of sulphur which it contains. It also presents an interesting example of a complex animal derivative, which may be artificially prepared in a very simple manner.

When olefiant gas is passed over anhydrous sulphuric acid, it is absorbed, and if the product be dissolved in water, neutralised with ammonia and evaporated, crystals of *isethionate of ammonia* are obtained—



$$C_2H_4 + SO_3 + NH_3 + H_2O = \underset{\text{Isethionate of ammonia.}}{NH_3.H_2O.C_2H_4SO_3}.$$

When this salt is moderately heated, it loses a molecule of water, and leaves taurine—



$$\underset{\text{Isethionate of ammonia.}}{NH_3.H_2O.C_2H_4SO_3} - H_2O = \underset{\text{Taurine.}}{C_2H_7NO_3S}.$$

Another characteristic ingredient of the bile is *cholesterine* * ($C_{26}H_{44}O$), a crystalline substance somewhat resembling the fats, and often deposited in large quantity in the form of biliary calculi. It has also been found in pease, wheat, and some vegetable oils.

The peculiar colouring matter of the bile has never been obtained in a pure state.

A peculiar substance called *glycogen*, or *animal starch* ($C_6H_{10}O_5$), has been found in the liver, and becomes speedily converted into sugar after death, by assimilating the elements of water.

The special function of the bile in the digestion of the food has not been explained, but from its strongly alkaline reaction it does not appear improbable that it assists in the digestion of fatty substances.

The *pancreatic juice* is another alkaline secretion, which differs from the bile in containing a considerable quantity of albumen, and is very putrescible. Its particular office in digestion appears to consist in promoting the conversion of the starchy portions of the food into sugar (p. 491), though it also has a powerful action upon the fats, causing them to form an intimate mixture, or emulsion, with water, and partly saponifying

* From *χολή*, *bile*; *στέαρ*, *fat*.

them. The digestion of the starch and sugar is completed by the action of the *intestinal fluid* in the further passage of the food through the intestines, so that when it arrives in the small intestines, all the soluble matters have become converted into a thin milky liquid called *chyle*, which has next to be separated mechanically from the insoluble portions, such as woody fibre, &c., which are excreted from the body.

This separation is effected in the small intestines by means of two distinct sets of vessels, one of which (the *mesenteric veins*) absorbs the dissolved starchy portions of the food, and conveys them to the liver, whence they are afterwards transferred to the right auricle of the heart. The other set of vessels (*lacteals*) absorbs the digested fatty matters, and conveys them, through the thoracic duct, into the subclavian vein, and thence at once into the right auricle of the heart.

From the right auricle this imperfect blood passes into the right ventricle of the heart, and is there mixed with the blood returned from the body by the veins, after having fulfilled its various functions in the system. The mixture, which has the usual dark-brown colour of venous blood, is next forced by the contraction of the heart, into the lungs, where it is distributed through an immense number of extremely fine vessels traversing the lungs, in contact with the minute tubes containing the inspired air, so that the venous blood is only separated from the air by very thin and moist membranes. Through these membranes the dark venous blood gives up the carbonic acid with which it had become charged by the oxidation of the carbon of the organs, in its passage through the body, and acquires, in return, about an equal volume of oxygen, which converts it into the bright crimson arterial blood. In this state it returns to the left side of the heart, whence it is conveyed, by the arteries, to the different organs of the body.

The chemistry of the changes effected and suffered by the blood in its circulation through the body is very imperfectly understood. One of its great offices is the supply of the oxygen necessary to oxidise the components of the various organs, and thus to evolve the heat which maintains the body at its high temperature. The results of the oxidation of these organs are undoubtedly very numerous; among them we may trace carbonic (CO_2), sulphuric (SO_3), phosphoric (P_2O_5), lactic ($C_3H_6O_3$), butyric ($C_4H_8O_2$), and uric ($C_5H_4N_4O_3$) acids, as well as urea (CH_4N_2O), and some other substances. The destroyed tissues must at the same time be replaced by the deposition, from the blood, of fresh particles similar to those which have been oxidised. In the course of the blood through the circulation, the above products of oxidation have to be removed from it—the carbonic acid by the lungs and skin—the sulphuric, phosphoric, and uric acids, and the urea, by the kidneys.

The various liquid secretions of the body, such as the bile, the saliva, the gastric juice, &c., have also to be elaborated from the blood during its circulation through the arteries, after which it returns, by the veins, to the heart, to have its composition restored by the matters derived from the food, and to be reconverted into arterial blood in the lungs.

When it is remembered that the body is exposed to very considerable variations of external heat and cold, a question occurs as to the provision made for maintaining it at its uniform temperature. This is effected through the agency of the fat which is deposited in all the organs of the body. Since fatty substances in general are particularly rich in carbon and hydrogen, their oxidation within the body would be attended with

the production of more heat than that of those parts of the organs which contain much nitrogen and oxygen. Accordingly, when the body is exposed to a low temperature, a larger quantity of its fat is consumed by the oxidising action of the blood, and a corresponding increase takes place in the amount of heat evolved, thus compensating for the greater loss of heat suffered by the body in the cooler atmosphere. Of course, in cold weather, when more oxygen is required to maintain the heat of the frame, a larger quantity of that gas is inhaled at each breath, on account of the higher specific gravity of the air, in addition to which we have the quickened respiration which always attends exposure to cold.

To supply this extra demand for carbon and hydrogen in cold weather, we instinctively have recourse to such substances as fat, starch, sugar, &c., which contain those elements in large proportion, and these aliments, free from nitrogen, are often spoken of as the *respiratory constituents* of food; whilst flesh, gluten, albumen, &c., which contain nitrogen, are styled the *plastic* elements of nutrition (πλάσσω, *to form*).

Bearing in mind that the food has a twofold office—to nourish the frame and to maintain the animal heat—it will be evident that a judiciously regulated diet will contain due proportions of those nitrogenous constituents, such as albumen, fibrine, and caseine, which serve to supply the waste of the organs, and of such non-nitrogenised bodies as starch and sugar, from which fat may be elaborated to sustain the bodily warmth.

The proportion which these two parts of the food should bear to each other will, of course, depend upon the particular condition of existence in the animal. Thus, for a growing animal, a larger proportion of the nitrogenised or plastic portion of food would be required than for an animal whose growth had ceased; and animals exposed to a low temperature would require more of the non-nitrogenised or heat-giving portions of the food.

Accordingly, we find that a man can live upon a diet which contains (as in the case of wheaten bread) five parts of non-nitrogenised (starch and sugar) to one part of nitrogenised food (gluten); whilst an infant, whose increasing organs require more nitrogenised material, thrives upon milk, in which this amounts to one part (caseine) for every four parts of the non-nitrogenised portion (milk-sugar and fat).

The inhabitants of cold climates consume, as is well known, much more oil and fat than those of the temperate and hot regions.

An examination of the composition of different articles of food affords us an explanation of the custom which experience has warranted, of associating particular varieties of food. Thus, assuming as our standard of comparison the composition of bread, which contains one of nutritive to five of heat-giving matter, the propriety of associating the following kinds of food will be appreciated:—

	Nutritive.	Heat-giving.
Beef	1	1·7
Potatoes, . . .	1	10
Ham, ...	1	3
Veal, ...	1	0·1
Mutton, . . .	1	2·7
Rice, ...	1	12·3

All muscular or mental exertion is attended with a corresponding

oxidation of the tissues of the frame, just as each movement of a steam-engine may be traced to the combustion of a proportionate quantity of coal under the boiler; and hence such exertion both creates a demand for food, and quickens the respiration to obtain an increased supply of oxygen.

Experiment has proved that the proportion which the oxygen consumed in respiration bears to the carbonic acid exhaled, depends very much upon the nature of the food. Thus an animal fed upon vegetable matters, such as starch and sugar (the oxygen in which exactly suffices to convert the hydrogen into water), will turn nearly all the inspired oxygen to account in the formation of carbonic acid, the volume of which will be nearly equal to that of the oxygen which disappears at each inspiration; but when flesh, or particularly fat, is consumed, much more of the inspired oxygen is required to convert the hydrogen of the food into water, so that the volume of the carbonic acid is far less than that of the oxygen consumed in respiration. When an animal has been kept for a length of time without food, the proportion between the volume of the carbonic acid and that of the oxygen consumed, is the same as if the animal were being fed upon a flesh diet, inasmuch as its own flesh alone is now supporting its respiration.

CHANGES IN THE ANIMAL BODY AFTER DEATH.

442. After the death of animals, just as after that of plants, their component parts are reduced to the primary forms from which they were derived, so that they may begin again at the foot of the ascending scale of life. Very soon after life is extinct, the atmospheric oxygen begins to induce a change in some of the nitrogenous constituents, and this change is soon communicated to all parts of the body, which undergo a putrefaction or metamorphosis, of which the ultimate results are the conversion of the carbon into carbonic acid, the hydrogen into water, the nitrogen into ammonia, nitrous and nitric acids, and the sulphur into sulphuretted hydrogen and sulphuric acid. The mineral constituents of the animal frame then mingle with the surrounding soil, and are ready to take part in the nourishment of plants, which construct the organic components of their frames from the carbonic acid and ammonia furnished by the putrefaction of the animal, and then serve in their turn as sustenance for animals whose respiration supplies the air with carbonic acid, and takes in exchange the oxygen eliminated by the plant.

The functions of the two divisions of animate nature are, therefore, perfectly reciprocal, and this relationship must be regarded as the foundation of economical agriculture.

If it were possible to prevent the change of the atmosphere, it is quite conceivable that a perpetual succession of plants and animals could be raised upon a given farm without any importation of food, provided that there was also no exportation. Or even, permitting an exportation of food, the succession of plants and animals raised upon the same land might be, at least, a very long one, if the solid and liquid excrements of the animals, to feed whom this exportation took place, were restored to the land upon which this food was raised. The explanation of this is, that the solid and liquid excrements of the animal contain a very large propor-

tion of the mineral constituents of the soil, in the very state in which they are best fitted for assimilation by the crop, and as long as the soil contains the requisite supply of mineral food, the plant can derive its organic constituents from the atmosphere itself.

Forasmuch, however, as the vegetable and animal food produced upon a farm is generally exported to feed the dwellers in towns, whose excrements cannot, without excessive outlay, be returned to the soil whence the food was derived, it becomes necessary for the agriculturist to purchase farm-yard manure, guano, &c., in order to prevent the exhaustion of his soil. A great manufacturing country, in which the majority of the inhabitants are congregated in very large numbers around a few centres of industry, at a distance from the land under tillage, is thus of necessity dependent for a considerable proportion of its food upon more thinly populated countries where manufactures do not flourish, to which it exports in return the produce of the labour which it feeds.

The parts of the frames of animals differ very considerably in their tendency to putrefaction. The blood and muscular flesh undergo this change most readily, as being the most complex parts of the body, whilst the fat remains unchanged for a much longer period, and the bones and hair will also resist putrefaction for a great length of time.

The comparative stability of the fat is observed in the bodies of animals which have been buried for some time in a very wet situation, when they are often found converted almost entirely into a mass of *adipocere*, consisting of the stearic and margaric acids derived from the fat.

When an animal body is thoroughly dried, it may be preserved unchanged for any length of time, and this is the simplest of the methods adopted for the preservation of animal food, becoming far more efficacious when combined with the use of some antiseptic substance such as salt, sugar, spice, or kreasote.

The preservative effects of salt and sugar are sometimes ascribed to the attraction exerted by them upon moisture, which they withdraw from the flesh, whilst spices owe their antiseptic power to the essential oils, which appear to have a specific action in arresting fermentative change, a character which also belongs to kreasote, carbolic acid, and probably to other substances which occur in the smoke of wood, well known for its efficacy in *curing* animal matter.

A process commonly adopted for the preservation of animal and vegetable food consists in heating them with a little water in tin canisters, which are sealed air-tight as soon as the steam has expelled all the air, and if the organic matter be perfectly fresh, this mode of preserving it is found very successful, though, if putrefaction has once commenced, to ever so slight an extent, it will continue even in the sealed canister, quite independently of the air.

Modern experiments have disclosed a great imperfection in our acquaintance with the conditions under which putrefaction takes place, and appear to indicate the presence in the atmosphere of some minute solid particles which appear to be minute ova or germs, and have the power of inducing the commencement of this change. It has been found that milk, for example, may be kept for a very considerable period without putrefying, if it be boiled in a flask, the neck of which is afterwards loosely stopped with cotton wool, whilst, if the plug of cotton wool be omitted, the other conditions being precisely the same, putrefaction will take place very speedily.

Perfectly fresh animal matters have also been preserved for a length of time in that state, in vessels containing air which has been passed through red-hot tubes with the view of destroying any living germs which might be present, and such substances have been found to putrefy as soon as the unpurified air was allowed access to them.

The extremes of the scale of animated existence would appear to meet here. The highest forms of organised matter, immediately after death, serve to nourish some of the lowest orders of living germs, these helping to resolve the complex matter into the simpler forms of carbonic acid, ammonia, &c., which are returned to the atmosphere, the great receptacle for the four chief elements of living matter.

ATOMIC WEIGHTS.

Element	Symbol	Weight
Aluminum	Al	27·5
Antimony	Sb	122
Arsenic	As	75
Barium	Ba	137
Bismuth	Bi	210
Boron	B	10·9
Bromine	Br	80
Cadmium	Cd	112
Cæsium	Cs	133
Calcium	Ca	40
Carbon	C	12
Cerium	Ce	92
Chlorine	Cl	35·5
Chromium	Cr	52·5
Cobalt	Co	59
Copper	Cu	63·5
Didymium	Di	96
Erbium	E	112·6
Fluorine	F	19
Glucinum	G	9·5
Gold	Au	196·6
Hydrogen	H	1
Indium	In	75·6
Iodine	I	127
Iridium	Ir	197·1
Iron	Fe	56
Lanthanium	La	92
Lead	Pb	207
Lithium	L	7
Magnesium	Mg	24·3
Manganese	Mn	55
Mercury	Hg	200
Molybdenum	Mo	96
Nickel	Ni	59
Niobium	Nb	94
Nitrogen	N	14
Osmium	Os	199
Oxygen	O	16
Palladium	Pd	106·5
Phosphorus	P	31
Platinum	Pt	197·1
Potassium	K	39·1
Rhodium	Ro	104·3
Rubidium	Rb	85·3
Ruthenium	Ru	104·2
Selenium	Se	79·5
Silicon	Si	28
Silver	Ag	108
Sodium	Na	23
Strontium	Sr	87·5
Sulphur	S	32
Tantalum	Ta	182
Tellurium	Te	129
Thallium	Tl	204
Thorinum	Th	238
Tin	Sn	118
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Tungsten	W	184
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Vanadium	V	51·3
Yttrium	Y	61·7
Zinc	Zn	65
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Gallium	Ga	69

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**** The names of minerals are printed in italics.*

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